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LIGHT SCATTERING AS A METHOD OF STUDYING POLYMERS

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INTRODUCTION

THE phenomenon of light scattering is well known. Beginning with the classic studies of Rayleigh^[1] at the end of the last century, its theory has been intensively developed as one of the branches of physical optics and molecular physics. Investigation of the scattering of light by a homogeneous ("optically empty") medium free from foreign particles shows that light can be propagated in such a medium only in the directions prescribed by the laws of geometric optics. In all other directions, the light waves emitted by the electrons of the molecules (or atoms) under the action of the field of the incident light wave are strictly coherent, and destroy one another by interference. Smoluchowski^[2] is responsible for the very important idea that complete homogeneity of media never exists, and that light scattering takes place at the microheterogeneities of the medium, or density fluctuations occurring in volumes that are small in comparison with the cube of the wavelength of the light; these arise from the chaotic thermal motion of the molecules. On the basis of these ideas, Einstein^[3] developed a quantitative thermodynamic theory of light scattering in liquids and solutions. In the latter theory, concentration fluctuations within volumes of the same order of magnitude play the major role. As applied to gases, Einstein's theory gives the same result as Rayleigh's original theory. The fundamental law derived in these theories—that the scattering intensity is inversely proportional to the fourth power of the wavelength of light—agrees with a number of light-scattering phenomena of everyday observation, such as the blue color

of the sky and of sea water, the red color of the sunrise, etc.

Further experimental and theoretical study of molecular light scattering (especially the studies of L. I. Mandel'shtam and G. S. Landsberg, Raman and Krishnan, Cabannes, and others) has made it possible to relate the measured characteristics of the scattered light to the physical parameters of the molecules in the matter scattering the light. Thus, the study of the intensity and polarization of the scattered light has become a method for studying the structural details of molecules. As applied to molecules of substances of low molecular weight, these problems have been treated in detail in a number of monographs.^[4-7] Relatively recently, within the last two decades, light scattering has also become one of the most important physical methods of studying the structure and properties of macromolecules, or polymer molecules. At present its application is not limited to determining molecular weights (which is a rather complicated problem in itself for polymers with $M \approx 10^6-10^7$), but includes the determination of such very important characteristics of a polymer as the dimensions and structure of its macromolecules, polydispersity of samples, compositional dispersion of copolymers, thermodynamic parameters of intermolecular interaction in solutions, etc. The relative experimental simplicity has facilitated the incorporation of the light-scattering method into the practice of many laboratories involved with polymer physics or physical chemistry. The vast experimental material that has accumulated in this field has been very little systematized. In particular, there exists not only no monograph literature on this prob-

lem in Russian, but not even any review literature. This review will endeavor to fill this gap to some extent. First place will be given here to the most important theoretical and experimental studies performed within the last 8–10 years, as well as to some problems requiring further development. This review is concerned with light scattering by molecular solutions of polymers. We shall not consider here such phenomena as light scattering by colloidal solutions, lattices, or gels, nor light scattering by polymer films, bearing in mind only the application of light scattering in studying the structure of individual macromolecules. The size of this review does not permit us to spend time on the peculiarities of the necessary apparatus or on certain important methodological problems that the reader can find in part in the specialized literature.^[8,9]

1. BASIC IDEAS OF THE THEORY OF LIGHT SCATTERING BY POLYMER SOLUTIONS

a) General Relations

We shall not give here a systematic presentation of the theory of light scattering by liquids and solutions. The pertinent material can be found in monographs.^[4-7] We shall give a résumé of the basic formulas and relations concerned with light scattering by polymer solutions, which are necessary for the further discussion of the theoretical and experimental studies.

Einstein^[3] derived the following relation for the intensity I of scattering from molecularly-disperse solutions:

$$I = \frac{\partial}{\partial c} \left(\frac{Hc}{RT} \right), \quad (1)$$

where c is the concentration of the solution, Π is the osmotic pressure, H is the optical constant of the solution, as will be defined below; and R and T have their usual meanings.

Since the osmotic pressure of the solution is given by the series

$$\frac{\Pi}{RT} = \frac{c}{M} + A_2c^2 + \dots, \quad (2)$$

in which M is the molecular weight of the solute, and A_2 is the second virial coefficient, (1) and (2) imply that

$$I = \frac{Hc}{\frac{1}{M} + 2A_2c + \dots}. \quad (3)$$

or

$$\frac{Hc}{I} = \frac{1}{M} + 2A_2c + \dots \quad (3a)$$

The general relation (3a) directly implies that one can determine the molecular weight M of a polymer from measurements of the scattering intensity I , if one knows the concentration c and the constant H of the solutions, by graphical extrapolation of the quantity Hc/I to $c = 0$.

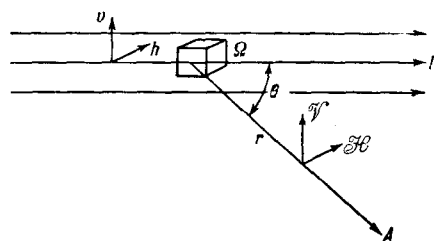


FIG. 1. Derivation of the general relations: components of the electric vector of the light wave in the primary (v, h) and scattered (v', h') beams, corresponding to scattered-light intensities I_v, I_h, v', h' .

We shall now consider some concrete cases of light-scattering measurements, and shall limit ourselves here for the time being to solutions of identical non-interacting particles. We shall assume that the solution is ideal ($A_2 = 0$), and that the scattering takes place without change of the wavelength of the incident light. That is, fluorescence does not take place.

Let the scattered light be observed at point A in the plane containing the primary (incident) and scattered beams (Fig. 1) at a distance r from the scattering volume Ω of the solution. Then the relation between the intensity $I(\theta)$ of the scattered light (the energy flux per unit area at point A) and that of the primary beam I_0 has the form

$$I(\theta) = \frac{16\pi^4}{\lambda_0^4} \frac{I_0 \Omega}{r^2} N_0 (\bar{\alpha})^2 P(\theta), \quad (4)$$

where N_0 is the number of solute particles per cm^3 of solution, $P(\theta)$ is some function of the scattering angle θ depending on the polarization of the light (in the incident and scattered beams) and the properties (dimensions, structure, and anisotropy) of the scattering particles, and $\bar{\alpha}$ is the mean excess polarizability of the scattering particles; λ_0 is the wavelength of the light in vacuo. Since in ordinary practice one makes relative measurements of the intensities $I(\theta)$ and I_0 , rather than absolute, the most important quantity is the reduced excess scattering intensity* I_θ , which equals

$$I_\theta = \frac{I(\theta)r^2}{I_0\Omega} = \frac{16\pi^4}{\lambda_0^4} N_0 (\bar{\alpha})^2 P(\theta). \quad (5)$$

The mean excess polarizability $\bar{\alpha}$ of the solute particles involves the refractive indices n of the solution and n_0 of the solvent (at low concentrations), through the well-known relation †

$$n^2 - n_0^2 = 4\pi N_0 \bar{\alpha}. \quad (6)$$

In very dilute solutions, $\Delta n = n - n_0 \ll n_0$. Hence, taking into account the fact that $c = N_0 M / N_A$, where N_A is Avogadro's number,

*In the foreign literature the reduced intensity is often called the Rayleigh ratio, and denoted by R_θ .

† Cf. [7], Vol. I, p. 376.

$$\bar{\alpha} = \frac{Mn_0}{2\pi N_A} \frac{dn}{dc}, \quad (7)$$

where

$$\frac{dn}{dc} = \frac{\Delta n}{c}$$

is the refractive increment of the solution. Using (5) and (7), we can derive

$$I_\theta = \frac{4\pi^2 n_0^2}{\lambda_0^4 N_A} \left(\frac{dn}{dc} \right)^2 cMP(\theta). \quad (8)$$

The factor standing in front of $cMP(\theta)$ in (8),

$$H = \frac{4\pi^2 n_0^2}{\lambda_0^4 N_A} \left(\frac{dn}{dc} \right)^2 \quad (9)$$

is a constant for a given polymer-solvent system, characterizing the optical properties of the solution. Hence we can write the following general relation for the reduced excess intensity:

$$I_\theta = HcMP(\theta). \quad (10)$$

b) Polarization Relations of Solutions of Particles of Different Types

Further, we shall assume that the scattering is observed at an angle θ from the incident light, and that the plane containing the incident and scattered beams is horizontal (as is usually the case experimentally). We shall designate the component of the reduced intensity of the scattered light belonging to light vibrations having a vertical electric vector by \mathcal{V} , and that having a horizontal electric vector by \mathcal{H} (Fig. 1). The subscripts v, h, or u affixed to these quantities will indicate the polarization state of the light in the incident beam: v and h for polarized incident light having a vibration direction respectively vertical or horizontal, and u when the incident light is natural (unpolarized).*

The six quantities $\mathcal{H}_u, \mathcal{H}_v, \mathcal{H}_h, \mathcal{V}_u, \mathcal{V}_v, \text{ and } \mathcal{V}_h$ are related by the four obvious relations

$$\left. \begin{aligned} \mathcal{H}_u &= \frac{1}{2} (\mathcal{H}_v + \mathcal{H}_h), \\ \mathcal{V}_u &= \frac{1}{2} (\mathcal{V}_v + \mathcal{V}_h), \\ \mathcal{H}_h &= (\mathcal{V}_v \cos^2 \theta + \mathcal{H}_v \sin^2 \theta), \\ \mathcal{H}_v &= \mathcal{V}_h. \end{aligned} \right\} \quad (11)$$

Thus, any two of these six quantities are independent.†

The total scattering intensity $I_{90^\circ u}$ with natural incident light can be expressed in terms of the quantities $\mathcal{V}_v, \mathcal{H}_h, \text{ and } \mathcal{V}_h$ as follows:

$$I_{90^\circ u} = \frac{1}{2} (\mathcal{V}_v + \mathcal{H}_h + 2\mathcal{V}_h).$$

The depolarization of scattered light consists in the appearance in the scattered light of an \mathcal{H} component, which is absent in the case of isotropic scattering, regardless of the polarization state of the incident light (at $\theta = 90^\circ$), owing to the fact that the vibrations in a light beam are transverse. When depolarization takes place, it is measured by the value Δ of the ratio of the \mathcal{H} and \mathcal{V} components of the scattered light. Three quantities, $\Delta_v, \Delta_h, \text{ and } \Delta_u$ are to be distinguished in accordance with the polarization state of the incident light:

$$\left. \begin{aligned} \Delta_v &= \mathcal{H}_v / \mathcal{V}_v, \\ \Delta_h &= \mathcal{H}_h / \mathcal{V}_h, \\ \Delta_u &= \frac{\mathcal{H}_v + \mathcal{H}_h}{\mathcal{V}_v + \mathcal{V}_h} = \frac{1 + \Delta_h}{1 + \Delta_v^{-1}}. \end{aligned} \right\} \quad (12)$$

Optical anisotropy of a particle consists in its having a polarizability that differs along the different axes of the particle. In distinction from isotropic particles, anisotropic particles in solution show depolarized scattering. The cases of scattering in solutions of isotropic and anisotropic particles, and small and large particles, essentially differ with regard to the angular distribution pattern (indicatrix) of the scattered light and its polarization. We shall treat these cases separately below.

The relations (12) show that only two of the three quantities, $\Delta_v, \Delta_h, \text{ and } \Delta_u$ are independent. This fact permits us to determine the quantity Δ_h , which is difficult to measure, from the measured values of Δ_v and Δ_u by using the last of the relations (12).

An analysis of the polarization state of the light scattered by a system of particles can be useful in establishing what type of particles they are. We must bear in mind that $\Delta_v, \Delta_h, \text{ and } \Delta_u$ are taken to mean the values of the degree of depolarization of the excess scattering of the solution obtained by extrapolation to infinite dilution ($c \rightarrow 0$) and measured at an angle of 90° with respect to the primary light beam.*

Small isotropic particles. In this case, the dipole moment of the particles induced by the field of the light wave coincides in direction with the field. Hence (see Fig. 1) with natural (u) and vertically polarized (v) incident light, $\mathcal{H}_u = \mathcal{H}_v = 0$, and $\mathcal{V}_v > 0$, while horizontally polarized (h) light, $\mathcal{H}_h = \mathcal{V}_h = 0$. Hence it follows that

$$\Delta_v = 0, \quad \Delta_u = 0, \quad \Delta_h = \frac{0}{0}.$$

Small anisotropic particles. In this case, the dipole moment of the particles induced by the field of the light wave forms an angle with the field direction (see [4,5] or [7], Vol. I). Consequently, the depolarized components $\mathcal{H}_v, \mathcal{V}_h, \text{ and } \mathcal{H}_h$ are no longer zero.

*The quantity Δ extrapolated to zero scattering angle will be denoted as $\Delta(0^\circ)$ below, e.g., $\Delta_v(0^\circ)$.

*Hereinafter we shall take the polarization direction of the light to mean the direction parallel to the electric vector of the light wave.

†The latter conclusion from the relations (11) is valid for particles of any dimensions, shape, and anisotropy (see below), provided that they are not optically active, and their axes are oriented at random with respect to the plane in which the scattering is being observed.[7]

Since from symmetry considerations $\mathcal{V}_h = \mathcal{H}_h$, then (taking into account the last of the relations (11)) all three depolarized components are equal to one another. Hence, (12) implies that

$$\Delta_h = 1, \quad \Delta_u = \frac{2\Delta_v}{1 + \Delta_v}.$$

Large isotropic particles. When the dimensions of the particles are comparable with the wavelength λ of the light, the latter induces a quadrupole moment in them, lying in the plane of observation of the scattering, as is shown in Fig. 2. At each given instant, two oppositely-directed dipoles (solid arrows) are produced in two cross-sections of the particle. They can be replaced by two dipoles (dotted arrows) emitting in the y direction (at an angle of 90° from the direction x of the light beam). The path difference of the scattering of the latter dipoles is $((\lambda/2) + a)$. Since $a \approx \lambda$, there is no longer total interference of the emission of these dipoles in the y direction, and a finite depolarized component remains, $\mathcal{H}_h > 0$. The quadrupole does not emit perpendicularly to its own plane, and hence, $\mathcal{V}_h = 0$. For the same reason, there is no quadrupole emission in the y direction with vertically polarized (v) incident light. That is, $\mathcal{H}_v = 0$, while the component \mathcal{V}_v of the scattered light contains only dipole emission.

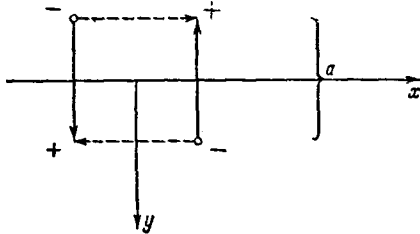


FIG. 2. The quadrupole moment induced in a large particle by the action of the field of the light wave. x = primary-beam direction, y = direction of observation of the scattering, a = transverse dimensions of the particle.

Here it follows from (12) that

$$\Delta_v = 0, \quad \Delta_h = \infty, \quad \Delta_u = \frac{\mathcal{H}_h}{\mathcal{V}_v} > 0.$$

\mathcal{H}_h and Δ_u increase with increasing particle dimensions, but if these dimensions do not exceed 0.2λ , the depolarization Δ_u still remains very small.

Large anisotropic particles. Just as for small anisotropic particles, all three depolarized components exist. However, owing to the quadrupole scattering, the component \mathcal{H}_h is greater than \mathcal{H}_v and \mathcal{V}_h , which are equal to one another. Hence the depolarization factor $\Delta_h > 1$, and it increases monotonically with the particle dimensions.

We shall now compare the depolarization factors for the four types of particles:

	Δ_v	Δ_h	Δ_u
small isotropic:	0	0/0	0
small anisotropic:	$\begin{matrix} >0 \\ <1 \end{matrix}$	1	$\begin{matrix} >0 \\ <1 \end{matrix}$
large isotropic:	0	∞	$\begin{matrix} >0 \\ <1 \end{matrix}$
large anisotropic:	$\begin{matrix} >0 \\ <1 \end{matrix}$	>1	$\begin{matrix} >0 \\ <1 \end{matrix}$

Thus, by measuring the depolarization factors Δ_v and Δ_u for vertically polarized and natural incident light, and calculating Δ_h from them, we can decide which of the four classes the scattering particles belong to. We note that only the factor Δ_v contains information on the intrinsic anisotropy of the particles (anisotropy of the substance), while the depolarization factor Δ_u arises to a considerable extent from the dimensions of the particles (via the scattering component \mathcal{H}_h , which is determined by the quadrupole emission).

2. SCATTERING IN SOLUTIONS OF SMALL PARTICLES

a) Small Isotropic Particles

We must consider particles to be small when their dimensions in solution do not exceed $\lambda/20$. Under this condition, the scattering from all elementary centers (oscillators) in the particle can be assumed to occur with the same phase, and the scattering intensity of the particle will be the sum of the scattering of all its oscillators.

Strictly speaking, only spherical particles of an isotropic substance are isotropic.

As was shown in Sec. 1 (b), depolarized scattering does not occur for small isotropic particles, and $\mathcal{H}_v = \mathcal{H}_h = \mathcal{H}_u = 0$.

If we affix the subscripts v, h, and u to the function $P(\theta)$ in accordance with the polarization of the incident light,* then for solutions of such particles,

$$P_v(\theta) = 1, \quad P_h(\theta) = \cos^2 \theta, \quad P_u(\theta) = \frac{1}{2}(1 + \cos^2 \theta). \quad (13)$$

Thus, in this case the scattering is given by the relations

$$I_{\theta v} = HcM \quad (14)$$

for incident light having the vibration direction vertical, and

$$I_{\theta u} = \frac{1}{2} HcM (1 + \cos^2 \theta) \quad (15)$$

for unpolarized incident light. In particular, in the case of greatest practical importance, with scattering

*The functions $P_v(\theta)$, $P_h(\theta)$, and $P_u(\theta)$ correspond to measurements of the total intensity of the scattered light. In those few cases involving measurement of the vertical component (\mathcal{V}) of the scattering alone, or the horizontal component (\mathcal{H}), the function $P(\theta)$ will have the necessary superscript [e. g., $P_v^{\mathcal{V}}(0^\circ)$].

at an angle $\theta = 90^\circ$ in unpolarized light,

$$I_{90^\circ u} = \frac{1}{2} HcM. \quad (16)$$

The scattering attenuates the primary light beam upon passing through a distance of l in the scattering medium according to the exponential law:

$$I(l) = I_0 e^{-\tau l}, \quad (17)$$

where τ is a quantity called the turbidity of the medium, having the dimensions of cm^{-1} (just as I_θ has). The turbidity τ can be calculated by integration of the scattering I_θ of the solution over all directions (over a sphere). Here we obtain

$$\tau = \frac{8\pi}{3} HcM, \quad (18)$$

which, combined with (16), implies that

$$\tau = \frac{16\pi}{3} I_{90^\circ u} \quad (19)$$

(here we assume that the turbidity of the pure solvent τ_0 is negligibly small in comparison with the turbidity τ of the solution; otherwise, we must take τ in (18) and (19) to mean the excess turbidity of the solution $\tau_{\text{exc}} = \tau - \tau_0$). It follows from (18) that we can determine M by measuring the turbidity (absorption) of solutions from the intensity of light transmitted by the solution. [10, 19]

b) Small Anisotropic Particles

In this case, depolarization of scattering takes place, and $\mathcal{H}_{V, h, u} \neq 0$.

We shall denote the principal polarizabilities of the particle in three mutually perpendicular directions by α_1 , α_2 , and α_3 . Then its optical anisotropy

$$\delta^2 = \frac{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2}{(\alpha_1 + \alpha_2 + \alpha_3)^2} \quad (20)$$

is related to the degree of depolarization Δ_u by the relation

$$\delta^2 = \frac{10\Delta_u}{6 - 7\Delta_u}. \quad (21)$$

For a solution of small anisotropic particles,

$$P_u(\theta) = \frac{1}{2} \frac{6 + 6\Delta_u}{6 - 7\Delta_u} \left[1 + \frac{1 - \Delta_u}{1 + \Delta_u} \cos^2 \theta \right]. \quad (22)$$

In the direction of the primary beam, $\theta = 0$, and

$$P_u(0^\circ) = \frac{1}{2} [P_v(0^\circ) + P_h(0^\circ)] = \frac{6}{6 - 7\Delta_u} = 1 + \frac{7}{10} \delta^2, \quad (23)$$

Here

$$\left. \begin{aligned} P_v(\theta) &= 1 + \frac{7}{10} \delta^2, & P_v^{\mathcal{V}0}(\theta) &= 1 + \frac{4}{10} \delta^2, \\ P_h(\theta) &= \frac{6}{10} \delta^2 + \left(1 + \frac{\delta^2}{10}\right) \cos^2 \theta, & P_h^{\mathcal{V}0}(\theta) &= \frac{3}{10} \delta^2. \end{aligned} \right\} \quad (24)$$

Since as a rule with solutions of small particles, one performs the scattering measurements at an angle of $\theta = 90^\circ$, $P(90^\circ)$ is especially important. Let the incident light have a vertical vibration direction. Then,

$$\left. \begin{aligned} P_v(90^\circ) &= \frac{3 + 3\Delta_v}{3 - 4\Delta_v}, \\ I_{90^\circ v} &= HcM \frac{3 + 3\Delta_v}{3 - 4\Delta_v}, \end{aligned} \right\} \quad (25)$$

and in measurements with unpolarized light,

$$\left. \begin{aligned} P_u(90^\circ) &= \frac{1}{2} \frac{6 + 6\Delta_u}{6 - 7\Delta_u}, \\ I_{90^\circ u} &= \frac{1}{2} HcM \frac{6 + 6\Delta_u}{6 - 7\Delta_u}. \end{aligned} \right\} \quad (26)$$

Thus, in comparison with the case of scattering from small isotropic particles [see (16)], Eq. (26) contains the factor $(6 + 6\Delta_u)/(6 - 7\Delta_u)$, which is called the depolarization factor (the Cabannes factor [11]).

The relation analogous to (18) for a solution of anisotropic particles has the following form:

$$\tau = \frac{8\pi}{3} HcM \frac{6 + 3\Delta_u}{6 - 7\Delta_u}, \quad (27)$$

Here we see that the coefficient relating τ to $I_{90^\circ u}$ is no longer equal to $16\pi/3$, as for isotropic particles, but depends on the anisotropy of the particles. In this case,

$$\tau = \frac{8\pi}{3} \frac{2 + \Delta_u}{1 + \Delta_u} I_{90^\circ u}. \quad (28)$$

3. SCATTERING IN SOLUTIONS OF LARGE PARTICLES

a) Large Isotropic Particles

When the dimensions of the particles in solutions are $\lambda/20$ or greater, the oscillators located at different points in the particle no longer oscillate in phase, and the waves that they scatter interfere. This leads to a decrease in the total scattering intensity. Understandably, the phase difference of the scattered rays is zero in the direction $\theta = 0$, and increases with the scattering angle θ . Under these conditions, the form of the function $P(\theta)$, which determines the angular scattering-intensity distribution of the particle (and the solution), must essentially depend on the distribution of the oscillators within the particle, i.e., on its internal structure.

The calculation of the function $P(\theta)$ for large particles is a very complicated problem. It has been solved by Mie [12] for the case of isotropic conductive spheres, and by Blumer [13] for dielectrics. The problem becomes considerably simpler when the mean refractive index n' of the particle is near the refractive index n_0 of the solvent, so that

$$4\pi(n' - n_0) \frac{D}{\lambda} \ll 1 \quad (29)$$

(here D is the maximum dimension of the particle, and $\lambda = \lambda_0/n_0$ is the wavelength in the liquid).

Inequality (29) usually holds for polymer solutions.*

*The volume of a polymer molecule swollen in a solvent greatly exceeds its "dry" volume, and hence, $(n' - n_0) \ll 1$.

This permits us to calculate $P_V(\theta)$ for certain specific structures; the most interesting of these to us are the sphere, the rod, and the Gaussian coil.

The function $P_V(\theta) = I_{\theta V}/I_0$, in full analogy to the relative intensity of scattering of X-rays by electrons in atoms,^[14,15] can be calculated as follows:^[16]

$$P_V(\theta) = \frac{1}{N^2} \sum_{p=1}^N \sum_{t=1}^N \left(\frac{\sin^2 \mu r_{pt}}{\mu r_{pt}} \right), \quad (30)$$

where $\mu = (4\pi/\lambda) \sin(\theta/2)$, and r_{pt} is the distance between the pair of emitters p and t in the particle. The double summation is performed over all possible pairs of emitters, the number of which in the particle is N . For flexible particles, we must average the summand over all conformations, taking into account the probability of a conformation having any given value for the distance r_{pt} . The factor $1/N^2$ is required for normalization, since $P_V(0^\circ) \equiv 1$, while for $\theta \rightarrow 0$, the double summation becomes N^2 . The summation in (30) has been calculated for particles of various structures. The results obtained for the structures of interest to us are given below.

Spherical particle (globular proteins). For a sphere of diameter D , the function $P_V(\theta)$ has the form^[17]

$$P_V(\theta) = \left[\frac{3}{z^3} (\sin z - z \cos z) \right]^2, \quad z = \frac{2\pi D}{\lambda} \sin \frac{\theta}{2}. \quad (31)$$

Rodlike particle (e.g., tobacco mosaic virus). For a rod having a length L much greater than its cross-section,^[18]

$$\left. \begin{aligned} P_V(\theta) &= \frac{1}{y} \text{Si}(2y) - \left(\frac{\sin y}{y} \right)^2, \\ \text{Si}(2y) &= \int_0^{2y} \frac{\sin t}{t} dt, \quad y = \frac{2\pi L}{\lambda} \sin \frac{\theta}{2}. \end{aligned} \right\} \quad (32)$$

Gaussian coil. For a randomly coiled linear (unbranched) macromolecule,^[14,15]

$$\left. \begin{aligned} P_V(\theta) &= \frac{2}{x^2} (e^{-x} - 1 + x), \\ x &= 16\pi^2 \frac{\overline{R^2}}{\lambda^2} \sin^2 \frac{\theta}{2}, \end{aligned} \right\} \quad (33)$$

where $\overline{R^2}$ is the mean square radius of gyration of the coil.*

Scattering functions have also been calculated for ellipsoids of rotation,^[20,21] cylinders,^[22] and thin disks.^[23]

A general property of the function $P_V(\theta)$ in all cases is that it becomes unity when $\theta = 0$. That is, $P_V(0^\circ) \equiv 1$. This obvious characteristic of the function $P_V(\theta)$ is a consequence of the fact mentioned above—there is no phase difference in the direction of the primary beam, there is no interference, and weakening of the scattering does not take place. Under-

*Here we assume averaging over all possible conformations of the macromolecule having the same total length L (as extended without altering the valence angles of the chain).

standably, the simple relation (19) does not hold for solutions of large particles. The relation between τ and L_{90° must be calculated with account taken of the function $P(\theta)$ for solutions of particles of the given type.

The course of the function $P_V(\theta)$ for particles of various shapes is shown in Fig. 3. We shall point out that for large isotropic particles of any shape,

$$P_h(\theta) = P_V(\theta) \cos^2 \theta$$

and hence,

$$P_u(\theta) = \frac{1}{2} P_V(\theta) (1 + \cos^2 \theta). \quad (34)$$

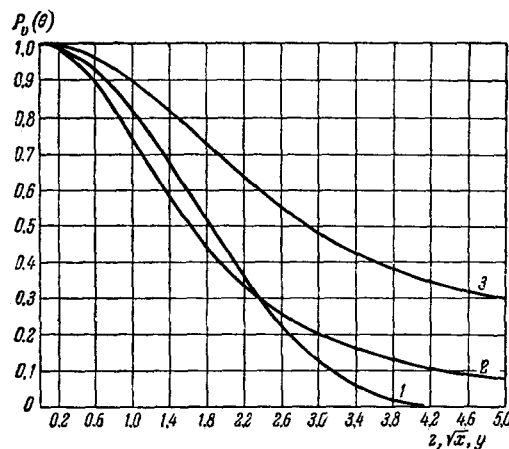


FIG. 3. Relation of the function $P_V(\theta)$ for intramolecular interference of scattering to the argument z , \sqrt{x} , or y , for particles of various structures: 1—spheres ($z = (2\pi D/\lambda) \sin(\theta/2)$); 2—coils ($x = 16\pi^2(\overline{R^2}/\lambda^2) \sin^2(\theta/2)$); 3—rods ($y = 2\pi(L/\lambda) \sin(\theta/2)$).

b) Large Anisotropic Particles

The problem of calculating the function $P(\theta)$ in this case is very complicated. For the simplest cases of a rodlike particle and a Gaussian coil, the solution has the following form.

Rodlike particle:^[24]

$$\begin{aligned} P_V^{70}(\theta) &= \left(1 - \frac{\delta}{\sqrt{2}} \right)^2 \left[\frac{\text{Si}(2y)}{y} - \frac{\sin^2 y}{y^2} \right] \\ &+ \frac{3\delta}{\sqrt{2}} \left(1 - \frac{\delta}{\sqrt{2}} \right) \left[\frac{\cos 2y}{2y^2} + \frac{\sin 2y}{4y^3} - \frac{1}{y^2} + \frac{\text{Si}(2y)}{y} \right] \\ &+ \frac{27}{16} \delta^2 \left[\frac{\sin 2y}{8y^5} - \frac{\cos 2y}{4y^4} + \frac{\sin 2y}{4y^3} + \frac{\cos 2y}{2y^2} - \frac{4}{3y^2} + \frac{\text{Si}(2y)}{y} \right], \end{aligned} \quad (35)$$

$$\begin{aligned} P_h^{70}(\theta) &= \frac{9}{8} \delta^2 \left\{ \frac{\cos 2y}{2y^2} + \frac{\sin 2y}{4y^3} - \frac{1}{y^2} + \frac{\text{Si}(2y)}{y} \right. \\ &- \frac{3}{4} \left[\frac{\sin 2y}{8y^5} - \frac{\cos 2y}{4y^4} + \frac{\sin 2y}{4y^3} + \frac{\cos 2y}{2y^2} - \frac{1}{3y^2} + \frac{\text{Si}(2y)}{y} \right] \\ &\left. - \frac{\cos \theta}{4} \left[\frac{5 \sin 2y}{8y^5} - \frac{5 \cos 2y}{4y^3} + \frac{\cos 2y}{2y^2} - \frac{8}{3y^2} + \frac{\text{Si}(2y)}{y} \right] \right\}, \end{aligned} \quad (36)$$

where y and $\text{Si}(2y)$ have their previous meanings (see (32)).

One can also find a more cumbersome expression for $P_h^{\mathcal{V}\theta}(\theta)$ in [24].

The polarizability of all the oscillators distributed along the axis of a rodlike particle is approximated here by an ellipsoid of rotation ($\alpha_2 = \alpha_3$), whose long axis (α_1) coincides with the axis of the whole particle. Thus, the optical anisotropy of the whole particle resembles that of the oscillators comprising it.

It is highly important that when $\theta = 0$, $P_V(0^\circ)$ is no longer unity, as for a large isotropic particle. In this case,

$$\begin{aligned} P_v^{\mathcal{V}\theta}(0^\circ) &= 1 + \frac{2}{5} \delta^2, & P_h^{\mathcal{V}\theta}(0^\circ) &= \frac{3}{10} \delta^2, \\ P_u(0^\circ) &= 1 + \frac{7}{10} \delta^2. \end{aligned} \quad (37)$$

Thus, at $\theta = 0$, where interference has no effect, anisotropy affects the scattering by large rodlike particles in the same way as for small particles (see (23)–(23)).

Gaussian coil. Let the polarizability of each link (monomer unit) of the chain be approximated by an ellipsoid of rotation having its long axis (α_1) in the direction of the link. Then one can derive [25]

$$\left. \begin{aligned} P_v^{\mathcal{V}\theta}(\theta) &= \frac{2}{x^2} (e^{-x} - 1 + x) + \frac{2\delta_0^2}{5N}, \\ P_h^{\mathcal{V}\theta}(\theta) &= \frac{3\delta_0^2}{10N}, \end{aligned} \right\} \quad (38)$$

where N is the number of links in the chain, and δ_0^2 is the anisotropy of the link. Since the number N of links is usually sufficiently large, $P_V^{\mathcal{V}\theta}(\theta)$ does not differ appreciably from the same quantity for a coil having isotropic links (see (33)). The second of the relations in (38) gives a value for the reduced intensity of the vertical scattering component (for a horizontal vibration direction of the incident light):

$$\mathcal{V}_{\theta h} = Hc \frac{M}{N} \cdot \frac{3\delta_0^2}{10} = HcM_0 \cdot \frac{3\delta_0^2}{10}. \quad (39)$$

Thus, the quantity $\mathcal{V}_{\theta h}$ does not depend on the degree of polymerization (M_0 is the molecular weight of the monomer unit), but is determined by the anisotropy of the link (monomer unit).

At $\theta = 0$, for a solution of Gaussian coils, we have

$$P_u(0^\circ) = 1 + \frac{7}{10} \frac{\delta_0^2}{N} \quad (40)$$

4. INTERPRETATION OF EXPERIMENTAL DATA

Usually, in undertaking light-scattering measurements, the experimenter already has an idea of the order of magnitude of the polymer molecules (molecular weight) from the value of the intrinsic viscosity of the solutions being studied. Accordingly, he selects a method for the light-scattering measurements. However, what one has learned about the characteristics of the function $P(\theta)$ permits one to determine the sequence and scope of the measurements within the limits of the light-scattering method alone.

It is evident from Eqs. (13) and (22) that for solutions of small particles, the function $P_u(\theta)$ is symmetrical with respect to the direction $\theta = 90^\circ$:

$$P_u(\theta) = P_u(180^\circ - \theta) \quad (41)$$

[the same is true of the function $P_V(\theta)$].

Hence, above all, symmetry of scattering is evidence that the solute particles are small in size. The subsequent analysis essentially differs for small and large particles.

a) Solutions of Small Particles

In this case, the classical method of light scattering in dilute solutions can give no information on the dimensions of polymer molecules.* To determine the molecular weight, one measures the intensity $I_{90^\circ u}$ (or $I_{90^\circ v}$) at several concentrations, and by graphic extrapolation to $c = 0$ determines

$$M = \left(\frac{Hc}{I_{90^\circ}} \right)_{c=0}^{-1}$$

b) Solutions of Large Particles. The Dissymmetry Method

There are two fundamental methods of interpreting the results of measurements for solutions of large particles—the dissymmetry method and the double-extrapolation method. We shall discuss them in turn as applied initially to solutions of isotropic particles.

A knowledge of the form of the function $P_V(\theta)$ permits us to calculate the value of the dissymmetry of scattering

$$|z| = \left(\frac{I_{45^\circ}}{I_{135^\circ}} \right)_{c=0}$$

for particles of any shape (structure) as a function of their relative dimensions D/λ . Figure 4 shows the value of $|z|$ for spherical, rodlike, and coillike particles. [19,26] As we see from Fig. 4, we can in some cases draw conclusions on the shape of the scattering particles from the value of the intrinsic dissymmetry $|z|$. Thus, a dissymmetry $|z| > 2.2$ excludes a rodlike shape of the particles, and $|z| > 4.5$ excludes a coiled structure. Conclusions of this sort, however, can be only qualitative in nature, and must be confirmed by supplementary data. The intrinsic value of the dissymmetry of the excess scattering

$$|z| = \left(\frac{I_{45^\circ}}{I_{135^\circ}} \right)_{c=0}$$

is usually determined graphically by extrapolation to $c = 0$ of the quantity $1/(z-1)$ taken from measurements on 5–8 solutions of decreasing concentrations.†

*Some possibilities have arisen here in connection with the phenomenon of critical opalescence (see[8]).

†It has been shown in[28] that the extrapolation of the quantity $1/(z-1)$ has the advantage over extrapolation of z that $1/(z-1)$ is a linear function of the concentration c in the range of low c .

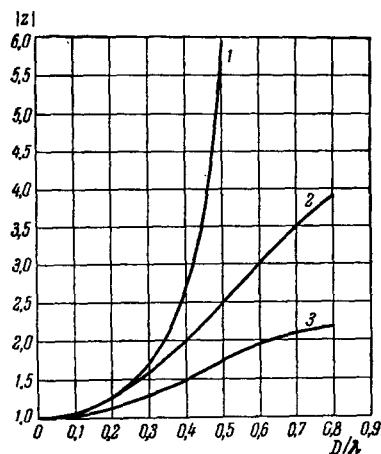


FIG. 4. Relation of the intrinsic scattering dissymmetry to the relative dimensions D/λ for particles of various structures: spheres (1), coils (2), and rods (3).

Using a suitable table or graph, we can determine from the quantity $|z|$ the relative dimensions of the particles in solution, as well as the factor $P_V^{-1}(90^\circ)$, which is necessary in calculating the molecular weight ([26], Fig. 5, Table). The latter is calculated by Eq. (10) by multiplying the reciprocal of the intercept of the plot of Ic/I_{90° against c by the factor $P_V^{-1}(90^\circ)$:

$$M = \left(\frac{Ic}{I_{90^\circ}} \right)_{c=0}^{-1} P_V^{-1}(90^\circ).$$

We should point out that for $|z| < 2$, the relative dimensions of coiled molecules can be determined^[27] by the following relation, which is sufficiently accurate in this region:

$$|z| = 1 + 6.565 \left(\frac{6\bar{R}^2}{\lambda^2} \right).$$

c) The Double-extrapolation Method

P. Debye^[15] was the first to point out a very im-

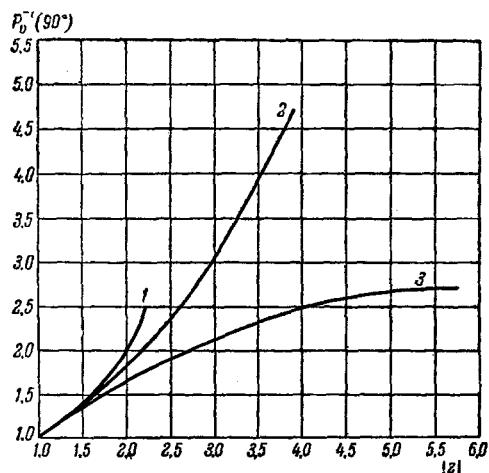


FIG. 5. The factor $P_V^{-1}(90^\circ)$ for particles of various shapes: rods (1), coils (2), and spheres (3), as a function of the intrinsic dissymmetry $|z|$.

portant characteristic of the function of intramolecular interference of light scattering $P_V(\theta)$. This characteristic consists in the fact that if one expands $P_V(\theta)$ or $P_V^{-1}(\theta)$ in a power series in the argument

$$\mu = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$$

near $\mu = 0$

$$P_c(\theta) = 1 - a_1\mu^2 + a_2\mu^4 - \dots, \quad (42)$$

$$P_V^{-1}(\theta) = 1 + a_1\mu^2 - a_2'\mu^4 + \dots \quad (42a)$$

the coefficient a_1 of the second term of the series characterizes the mean dimensions of the particle independently of its shape.

In fact, an expansion of $\sin \mu r_{pt}$ in a power series in the quantity (μr_{pt}) in the general expression for $P_V(\theta)$ (Eq. (30)) gives

$$\begin{aligned} P_c(\theta) &= \frac{1}{N^2} \sum_{p,t=1}^N \left[\frac{1}{\mu r_{pt}} \left(\mu r_{pt} - \frac{\mu^3 r_{pt}^3}{6} + \dots \right) \right] \\ &= 1 - \frac{\mu^2}{6N^2} \sum_{p,t=1}^N (r_{pt}^2 + \dots). \end{aligned} \quad (43)$$

The quantity r_{pt} can be represented as the vector difference between the distances r_{ic} from the corresponding emitters to the center of inertia of the particle; then

$$\overline{r_{pt}^2} = (\overline{r_{pc} - r_{tc}})^2 = \overline{r_{ic}^2} - 2(\overline{r_{pc}r_{tc}}) + \overline{r_{ic}^2}. \quad (44)$$

The mean square radius of gyration \overline{R}^2 of the particle is given by the expression

$$\overline{R}^2 = \frac{1}{N} \sum_{i=1}^N r_{ic}^2. \quad (45)$$

Let us take into account the fact that, owing to symmetry for rods, spheres, disks, ellipsoids, and similar structures, the scalar product $r_{pc} \cdot r_{tc}$ is zero on the average. Then, the double summation in (43) gives $2N^2\overline{R}^2$ and

$$P_V(\theta) = 1 - \frac{1}{3} \mu^2 \overline{R}^2 + \dots \quad (46)$$

For Gaussian chains,

$$\overline{r_{pt}^2} = |t-p| b^2 \quad \text{и} \quad \overline{R}^2 = \frac{1}{6} N b^2,$$

where b is the length of the chain unit.^[8] The double summation of the quantity $|t-p|$ gives $N^3/3$, and for coiled molecules we obtain

$$P_V(\theta) = 1 - \frac{\mu^2}{3} \frac{N b^2}{6} + \dots = 1 - \frac{1}{3} \mu^2 \overline{R}^2 + \dots$$

Thus, the coefficient of the second term in the series expansion of $P_V(\theta)$ or $P_V^{-1}(\theta)$ in powers of μ^2 is independent of the structure of the particle, and is $1/3 \overline{R}^2$.

This fundamental characteristic of the function $P_V(\theta)$ is extremely important, and in principle, it makes it possible in the light-scattering method to do

the following. If we plot $P_V^{-1}(\theta)$ against $\sin^2(\theta/2)$, then at sufficiently low angles θ we obtain a straight line whose slope gives the radius of gyration of the particle, independently of any model concepts on its structure.

This characteristic of the function $P_V(\theta)$ (together with the above-mentioned property that $P_V(0^\circ) \equiv 1$) is the basis of a method proposed by Zimm^[28,29] for interpreting light-scattering data, which has been called the double-extrapolation method. In following this method, one measures $I_{\theta V}$ for a series of concentrations and different scattering angles θ , and then plots a graph (Zimm plot) of the quantity $Hc/I_{\theta V}$ as a function of the complicated argument $\sin^2(\theta/2) + kc$. The constant k is chosen so that kc_{\max} will be of the order of several times unity. Then one extrapolates to $c = 0$ from all the measurements at each of the angles θ , and extrapolates to $\theta = 0$ from all the measurements at each of the concentrations c . The net obtained is shown in Fig. 6. The intercept

$$A_0 = \left(\frac{Hc}{I_{\theta V}} \right)_{\substack{c=0 \\ \theta=0}}$$

is obtained as the point of intersection of the two extrapolated curves ($c = 0$ and $\theta = 0$), and gives the true value of the molecular weight

$$M = \left(\frac{Hc}{I_{\theta V}} \right)_{\substack{c=0 \\ \theta=0}}^{-1} = \frac{1}{A_0}. \quad (47)$$

Thus, the accuracy of determination of M is considerably increased. According to (34), for measurements with natural light,

$$M = \left(\frac{Hc(1 + \cos^2 \theta)}{2I_{\theta u}} \right)_{\substack{c=0 \\ \theta=0}}^{-1}.$$

According to (46), the initial slope s_0 of the curve $(Hc/I_{\theta V})_{c=0}$ in the double-extrapolation graph (Zimm plot) gives the radius of gyration R^2 of the particles:

$$\frac{s_0}{A_0} = \frac{1}{3} R^2 \frac{16\pi^2}{\lambda^2}. \quad (48)$$

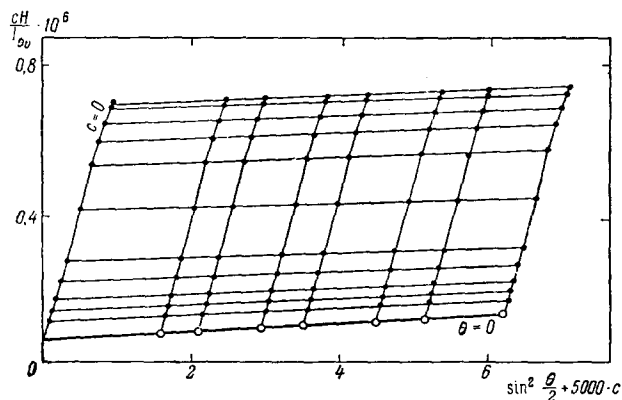


FIG. 6. Double-extrapolation graph (Zimm plot) for solutions of a poly-2,5-dichlorostyrene fraction ($M = 16.7 \times 10^4$) in dioxane^[30].

For Gaussian coils, $R^2 = h^2/6$, and (48) gives for the mean distance $(h^2)^{1/2}$ between the ends of the coil:

$$\frac{h^2}{\lambda^2} = \frac{9}{8\pi^2} \frac{s_0}{A_0}. \quad (49)$$

The relation of the reciprocal Debye function $P_V^{-1}(\theta)$ for Gaussian coils to its argument

$$x = 16\pi^2 \frac{R^2}{\lambda^2} \sin^2 \frac{\theta}{2}$$

[see (33)] is shown in Fig. 7. The monotonic curve of the function $P_V^{-1}(\theta)$ consists of an initial and an asymptotic branch.^[29] The initial tangent corresponds to the equation $(1 + x/3)$, while the equation of the asymptote is $(0.5 + x/2)$.

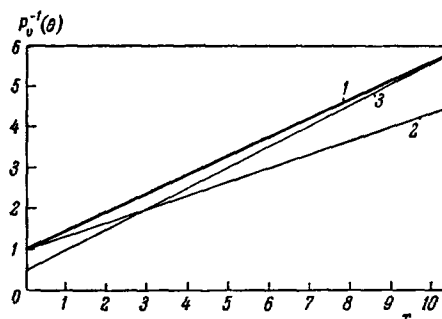


FIG. 7. Graph of the reciprocal Debye scattering function $P_V^{-1}(\theta)$ for Gaussian coils,

$$x = 16\pi^2 (R^2/\lambda^2) \sin^2(\theta/2).$$

1—The function $P_V^{-1}(\theta)$; 2—initial tangent; 3—asymptote.

It is interesting to compare the asymptotic behavior of the scattering functions $P_V^{-1}(\theta)$ (for large values of the arguments) for particles of different shapes. We can derive from Eqs. (31)–(33): for spherical particles

$$P_V^{-1}(\theta) \approx \frac{2}{9} \left(4\pi \frac{D}{\lambda} \right)^4 \sin^4 \frac{\theta}{2}, \quad (50)$$

for rodlike particles

$$P_V^{-1}(\theta) \approx \frac{1}{\pi} \left(4\pi \frac{L}{\lambda} \right) \sin \frac{\theta}{2} \quad (51)$$

and for Gaussian coils

$$P_V^{-1}(\theta) \approx \frac{1}{3} \left(4\pi^2 \frac{h^2}{\lambda^2} \right) \sin^2 \frac{\theta}{2}. \quad (52)$$

The asymptotic behavior of the $P_V(\theta)$ functions comes into effect at sufficiently large particle dimensions and at scattering angles that are not too small ($\theta \approx 180^\circ$). We see by comparing (50)–(52) that an experimental study of the behavior of the quantity $(Hc/I_{\theta V})_{c=0}$ as a function of the argument $\sin(\theta/2)$ can aid in solving the problem of the shape of a particle, since in the cited three cases $P_V^{-1}(\theta)$ is respectively proportional to $\sin^4(\theta/2)$, $\sin(\theta/2)$, and $\sin^2(\theta/2)$.

d) Solutions of Large Anisotropic Particles

This case is considerably harder to interpret. As has been noted above, for large anisotropic particles, $P_V(0^\circ) \neq 1$, and in principle, the double-extrapolation method does not give a correct value for the molecular weight. According to (20), the extreme values of the optical anisotropy δ^2 of a particle are 2 (when $\alpha_2 = \alpha_3 = 0$) and $1/2$ (when $\alpha_1 = 0$, and $\alpha_2 = \alpha_3$). Here, the function $P_V^{7/2}(0^\circ)$ for a rodlike particle has values of 1.8 and 1.2, respectively [see (37)]. Thus, neglect of anisotropy can give rise to errors of from 20% to 80% in determining the molecular weight of rodlike particles. We can obtain the value of δ^2 , which is necessary in calculating M correctly, by measuring the depolarization of the excess scattering Δ_V with double extrapolation: $0 \rightarrow 0$ and $c \rightarrow 0$ (for the quantities \mathcal{E}_V and \mathcal{V}_V separately; for more details, see [30]). Using the relations (37), we can easily obtain

$$\Delta_V(0^\circ) = \frac{3\delta^2}{10 + 4\delta^2}, \quad (53)$$

whence

$$\delta^2 = \frac{10\Delta_V(0^\circ)}{3 - 4\Delta_V(0^\circ)}. \quad (54)$$

Relations (53) and (54) are valid for particles of any dimensions and shape.

Upon determining the value of δ^2 from the depolarization $\Delta_V(0^\circ)$, we can calculate the molecular weight of rodlike particles by using the ordinary double-extrapolation method:

$$M = \left(\frac{Hc}{\mathcal{V}_V^{7/2}} \right)_{c=0, \theta=0}^{-1} \left(1 + \frac{2}{5} \delta^2 \right)^{-1} = \frac{1}{A_0} \left(1 + \frac{2}{5} \delta^2 \right)^{-1}. \quad (55)$$

For measurements in natural light,

$$M = \left(\frac{cH(1 + \cos^2 \theta)}{2I_{\theta u}} \right)_{c=0, \theta=0}^{-1} \left(1 + \frac{7}{10} \delta^2 \right)^{-1} = \frac{1}{A_0} \left(1 + \frac{7}{10} \delta^2 \right)^{-1},$$

while δ^2 is calculated from $\Delta_V(0^\circ)$ by relation (53).

Figure 8 shows the relation of the scattering dissymmetry

$$|z| = \left(\frac{I_{45^\circ u}}{I_{135^\circ u}} \right)_{c=0}$$

for rodlike particles to their relative length L/λ for various values of δ ($\alpha_2 = \alpha_3$). Upon determining δ , we can use this graph to find the dimensions of the particles from the measured scattering dissymmetry (see also [30]).

For Gaussian coils of sufficiently large molecular weight, $P_V^{7/2}(0^\circ)$ is near unity [see (38)], and the double-extrapolation method gives correct values of M and h^2/λ^2 .

5. DIMENSIONS AND FLEXIBILITY OF MACROMOLECULES

Light scattering, along with small-angle X-ray scattering, is one of the direct methods of determining the dimensions of macromolecules in solution.

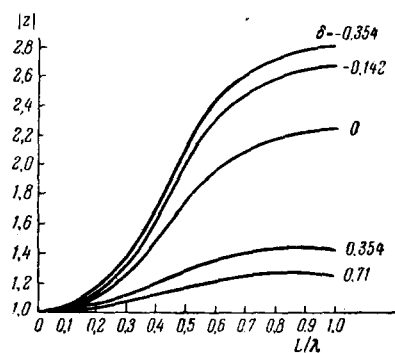


FIG. 8. The relation of the intrinsic scattering dissymmetry $|z|$ of solutions of rodlike particles to their relative length L/λ for various values of the anisotropy δ . [24]

At present, systematic measurements of the dimensions of macromolecules in solution are made for the following basic reasons: to find the nature of the relation of the dimensions to the molecular weight, the effect of thermodynamic polymer-solvent interactions on the dimensions, and the effect of the temperature on the dimensions. While there is a rather large amount of experimental data on the first problem, the studies on the second and third problems have thus far remained very few in number. Furthermore, it is precisely these problems that are the most complex.

Figure 9 shows the relation of the coil dimensions $(\bar{h}^2)^{1/2}$ to the second virial coefficient A_2 of the solutions for four fractions of polymethylmethacrylate (with M from 0.5×10^6 to 6.6×10^6), as obtained in [31]. The correlation between $(\bar{h}^2)^{1/2}$ and A_2 is obvious. As A_2 increases, the dimensions of the coils can increase twofold (or further) with respect to their dimensions for $A_2 = 0$.

The correlation between $(\bar{h}^2)^{1/2}$ and A_2 is based on osmotic effects—the increase in the swelling coefficient of the coil

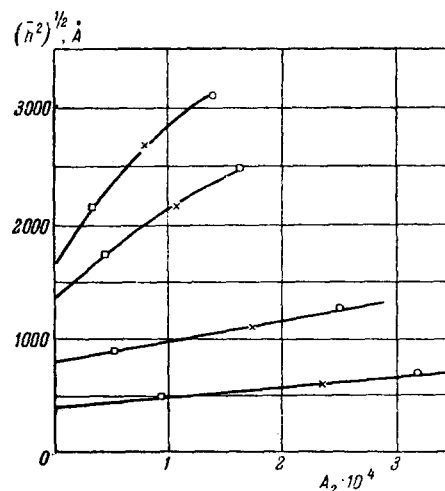


FIG. 9. Relation of the coil dimensions $(\bar{h}^2)^{1/2}$ for four fractions of polymethylmethacrylate to the second virial coefficient A_2 of the solutions [31] (M from 0.5×10^6 to 6.6×10^6).

$$\alpha = \left(\frac{\bar{h}^2}{h_0^2} \right)^{1/2}$$

as the thermodynamic interaction of the segments (links) of the coil with the solvent increases ($(\bar{h}_0^2)^{1/2}$ is the size of the coil in an ideal solvent, for which $A_2 = 0$).

Temperature change has a different effect on the coil dimensions in good and in poor solvents. In good solvents, the thermodynamic interaction of the polymer with the solvent varies very little with temperature. Hence, the important factor here is the variation in the short-range interaction in the chain.^[32] The result of this variation is that the coil dimensions $(\bar{h}^2)^{1/2}$ decrease with increasing temperature in good solvents. Such a decrease has been repeatedly observed experimentally (see, e.g. ^[33]). In poor solvents, the variation in the short-range interaction also takes place. However, here the prevailing factor is the increase in the polymer-solvent interaction. The sharp increase in the swelling of the coil initially results in an increase in the coil dimensions with rising temperature.^[33,34] With further temperature rise, this increase in $(\bar{h}^2)^{1/2}$ must slacken off and give way to a decrease when the variation in the short-range interaction in the chain begins to predominate.

Light-scattering measurements made over small temperature ranges (as a rule not exceeding 30–40°) have generally confirmed the simple notions presented above on the nature of the variation of the coil dimensions in good and in poor solvents.

An experiment performed recently by Reiss and Benoit^[35] has shown that the variation of the coil dimensions over a broad temperature range does not fit the relatively simple pattern given above. Figure 10 shows the results of measuring $(\bar{R}^2)^{1/2}$ for polystyrene molecules ($M = 2.5 \times 10^6$) in decalin from 31°C (the Θ -point) to 120°C. The existence of a second region of increasing dimensions (from 90° to 120°C) is rather hard to explain, even though the variation in $(\bar{R}^2)^{1/2}$ agrees with the trend in A_2 in the same temperature range. An analogous variation in $(\bar{R}^2)^{1/2}$ has also been established in toluene and xylene, which are good solvents.

The authors of ^[35] suggest that for polystyrene the complex temperature-dependence of the coil dimensions involves partial ordering in the positions of the benzene rings, leading to local helix formation in the chain, while this vanishes at high temperatures. The result of ^[35] has been obtained again in a less distinct form,^[36] but here it contrasted with a smooth increase in the intrinsic viscosity $[\eta]$ over the same temperature range. The data of ^[35,36] show that the temperature-dependence of the coil dimensions apparently is more complex in nature than was previously supposed.

Quite probably, the general ideas presented above must be essentially modified for actual polymers, depending on their chemical structure, in particular on

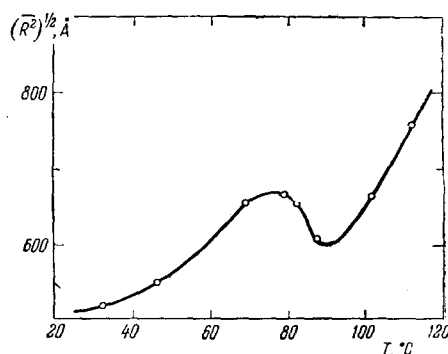


FIG. 10. Temperature-dependence of the mean radius of gyration $(\bar{R}^2)^{1/2}$ for polystyrene coils ($M = 2.5 \times 10^6$) in decalin.^[35]

the composition of the side groups on the chain. This interesting problem requires further special studies.

The relation of the coil dimensions $(\bar{h}^2)^{1/2}$ to the molecular weight has been subjected to many studies (see, e.g., ^[33,34,37,38]). One of the most important results of such studies is the establishment of the fact that the predicted statistical theory of proportionality: $(\bar{h}^2)^{1/2} \sim M^{1/2}$, is not valid in non-ideal (good) solvents, as $(\bar{h}^2)^{1/2}$ increases more rapidly than $M^{1/2}$. This proves directly that the swelling coefficient α of the coils increases with the molecular weight, and hence

$$\left(\frac{\bar{h}^2}{h_0^2} \right)^{1/2} = \alpha(M),$$

in agreement with the predictions of the thermodynamic theory of polymer solutions.^[32] The cited studies (and others) show that the exponent a in the relation

$$(\bar{h}^2)^{1/2} = KM^a$$

lies between the limits $0.5 < a < 0.6$ for good solvents. Thus, if N is the degree of polymerization,

$$\bar{h}^2 = K'N^{1+\epsilon}, \quad (56)$$

where $0 < \epsilon < 0.20$.^[32]

In ideal solvents (for which $A_2 = 0$), $a = 0.5$.^[34,39-46]

Flory's theory^[32] predicted that the coefficient Φ is a universal constant in the well-known Flory-Fox equation

$$[\eta] = \Phi \frac{(\bar{h}^2)^{3/2}}{M} \quad (57)$$

relating the intrinsic viscosity $[\eta]$, $(\bar{h}^2)^{1/2}$, and M . Subsequent measurements^[47] have shown in a number of cases appreciable deviations of Φ from the mean value $\Phi = 2.1 \times 10^{23} \text{ mole}^{-1}$ that Flory originally established from various measurements. At the same time, a theoretical treatment^[48] has shown that the interaction of the macromolecules with the solvent can appreciably alter Φ by affecting the nature of the distribution of the links within the coil: Φ varied from 2.8×10^{23} in an ideal solvent to 1.6×10^{23} in a good solvent. It is now known that other factors besides the interaction with the solvent (swelling), in particular,

increased rigidity of the chain,^[48] also alter the coefficient Φ by affecting the hydrodynamic interaction of the links in the coil. Hence, anomalous values of Φ from measurements of the viscosity $[\eta]$ and light scattering ($\overline{h^2}$ and M) are a sign of special properties in the chains leading to disagreement (as compared with the usual relation) between the optical ($\overline{h^2}$) and hydrodynamic ($[\eta]$) dimensions of the coils. We encounter such a situation, e.g., in studying the light scattering of polyvinyl naphthalene, cellulose derivatives, and DNA.

The nature of relation of $(\overline{h^2})^{1/2}$ to M in the region of transition from short rigid chains (oligomers) to Gaussian coils ($M \approx 10^4$) is of considerable interest. However, this region is inaccessible to the classical light-scattering method, owing to the small size of the scattering particles. Certain researchers have determined $(\overline{h^2})^{1/2}$ in this region from measurements of $[\eta]$, using Eq. (57).^[50] The vulnerable point of these studies is the use here of the value of Φ obtained in the region of large values of M . As is known, for short (rigid) chains, the coefficient Φ differs from this value.^[51,52,49] The possible deviation of $(\overline{h^2})^{1/2}$ in the region of small M from the law, $(\overline{h^2})^{1/2} \sim M^a$, which is valid for large M , is apparently small. Thus, it can be masked by the cited variation in Φ .

As has been stated, in non-ideal solvents, both the short-range and the long-range interactions in the chains vary with increasing T . This complicates the interpretation of the results obtained. The measurement of $(\overline{h_0^2})^{1/2}$ in several Θ -solvents* at various temperatures makes it possible to distinguish the temperature-variation of the short-range interaction alone. Such an experiment has been carried out by Schulz and Kirste^[53] with a polymethylmethacrylate fraction ($M = 2.1 \times 10^5$) in nine Θ -solvents over the temperature range from -40° to $+60^\circ\text{C}$. Here the Θ -point was determined in each case by light scattering (interpolation of A_2), while the variation in dimensions was determined from the value of $[\eta]_\Theta$. According to (57), the latter is more sensitive to variations in the coil dimensions than the scattering dissymmetry, which is proportional to $\overline{h^2}$. The result, which is shown in Fig. 11, indicates an increase in $[\eta]$, and hence of $(\overline{h_0^2})^{1/2}$, with the temperature. This is somewhat unexpected, since we might suppose that the decrease in the hindrance of rotation of the links in the chain with increasing T would lead to an increase in the flexibility of the chain and a decrease in its dimensions $(\overline{h_0^2})^{1/2}$. The authors of^[53] point out two possible reasons for the increase in $(\overline{h_0^2})^{1/2}$ with T that they found: asymmetry of the internal-rotation potential, and competition between the increase in freedom of rotation of the side-chain groups and of the main links of the chain. In any case, the result of this study (as of the above-

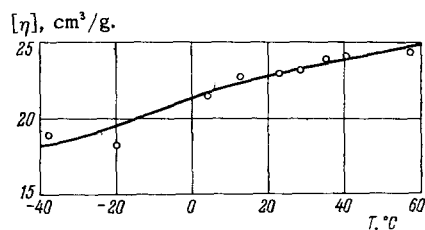


FIG. 11. Temperature-dependence of the intrinsic viscosity $[\eta]_\Theta$ in an ideal solvent for a polymethylmethacrylate fraction ($M = 2.1 \times 10^5$).^[53]

discussed study of Reiss and Benoit^[35] with polystyrene) shows that the variation of the coil dimensions with the temperature is a very complex phenomenon, and requires further study.

The authors of^[53] discern in the smooth course of the curve in Fig. 11 a proof that the solvent exerts no specific effect on the dimensions of polymer coils. This conclusion cannot be true in general. A number of studies^[54,55] have considered the possibility of such an effect. It was shown in^[56] that the variation in $[\eta]$ in Θ -solvents of differing chemical composition at one given Θ temperature can be as great as 20% for polystyrene. An analogous result has been obtained for coils of hexene-1-polysulfone by determining $(\overline{R_0^2})^{1/2}$ directly by the light-scattering method.^[57] The value of $(\overline{R_0^2})^{1/2}$ was measured by the double-extrapolation method in three Θ -solvents: n-hexyl chloride and two mixtures of butanone with isopropyl alcohol.* They obtained for a sample having $M = 7 \times 10^5$ in the first solvent $(\overline{R_0^2})^{1/2} = 600 \text{ \AA}$, and in the two other solvents 500 \AA (the values of $[\eta]_\Theta$ differed correspondingly). This important and interesting problem also requires thorough study. Here, naturally, one must determine $(\overline{h_0^2})^{1/2}$ in various Θ -solvents by the light-scattering method (rather than viscosity) to exclude the alternative possibility that the coefficient Φ in Eq. (57), rather than the quantity $(\overline{h_0^2})^{1/2}$, depends on the specific polymer-solvent interaction.

In ideal solvents, for which $A_2 = 0$, the long-range interaction forces in the macromolecule (repulsion of remote segments along the chain upon fortuitous approach) are compensated by the interaction with the solvent. Consequently, the unperturbed dimensions of the coils $(\overline{h_0^2})^{1/2}$ are established. The latter are determined only by the "skeletal" effects in the chain (short-range interaction), which limit its flexibility. Hence, the ratio $(\overline{h_0^2}/\overline{h_{f,r}^2})^{1/2}$ of the unperturbed

*A correct determination of the value of M in a mixture of solvents having refractive indices n'_0 and n''_0 requires that the following condition be obeyed:

$$\frac{dn}{dc} \gg (n'_0 - n''_0).$$

The determination of the coil dimensions makes no limitations on the choice of components of a mixed solvent^[196] (see also^[1], Chap. III, Sec. 5).

*We shall use the term " Θ -solvent" together with the term "ideal solvent" for solvents in which $A_2 = 0$.

Table I. The relative unperturbed coil dimensions $(\overline{h_0^2}/\overline{h_{i.r.}^2})^{1/2}$ of various polymers in solution (A is the length of the statistical segment of the chain, and S is the number of monomer units per segment A). Methods of determining $(\overline{h_0^2}/\overline{h_{i.r.}^2})^{1/2}$: L — light scattering in a Θ -solvent, V — viscosity in a Θ -solvent, LA₂ — light scattering in a good solvent and second virial coefficient, VA₂ — viscosity in a good solvent and second virial coefficient






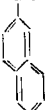
Polymer	Monomer unit	$(\overline{h_0^2}/\overline{h_{i.r.}^2})^{1/2}$	A · 10 ⁸ , cm	S	Method
1. Polyethylene	—CH ₂ —CH ₂ —	2.3—2.4	20.8	8.3	VA ₂ ⁵⁹ , LA ₂ ⁶⁰
2. Polypropylene	—CH ₂ —CH— CH ₃	2.4	21.7	8.6	LA ₂ ⁶¹
3. Polyisobutylene	—CH ₂ —C— CH ₃	2.2	18.3	7.3	L ⁶² , V ⁶³⁻⁶⁵
4. Polyvinylbromide	—CH ₂ —CH— Br	1.9	13.6	5.4	L ⁶⁶
5. Polyvinylchloride	—CH ₂ —CH— Cl	2.8	29.6	11.7	LA ₂ ⁶⁷
6. Polyvinylbenzoate	—CH ₂ —CH— O C=O 	2.65	26.5	10.5	L ⁶⁸
7. Poly-4-vinylpyridine	—CH ₂ —CH— 	2.4	21.7	8.6	V ⁶⁹
8. Polystyrene	—CH ₂ —CH— 	2.2—2.4	20.0	7.9	L ^{33, 47, 62, 34, 39, 40, 70} V ⁶⁴
9. Poly-2,5-dichlorostyrene	—CH ₂ —CH— 	2.45	22.7	9.0	L ⁴⁰
10. Poly-3,4-dichlorostyrene	—CH ₂ —CH— 	2.9	31.7	12.6	L ⁴²
11. Poly-β-vinyl-naphthalene	—CH ₂ —CH— 	3.2	38.7	15.4	L ⁴¹
12. Polyacrylic acid	—CH ₂ —CH— OH—C=O	1.8	12.2	4.9	LA ₂ ⁷¹ VA ₂ ⁵⁹
13. Polyacrylonitrile	—CH ₂ —CH— C≡N	3.2—2.6	31.7	12.6	LA ₂ ⁷¹ VA ₂ ⁵⁹
14. Polyvinylacetate	—CH ₂ —CH— CH ₃ —C—O O	2.1—2.3	17.4	6.9	L ⁷² , V ⁷³
15. Polymethylmethacrylate	—CH ₂ —C— CH ₃ CH ₃ O—C=O	1.8—2.0— 2.2	15.1	6.0	L ^{43, 75, 76}
16. Polyethylmethacrylate	—CH ₂ —C— CH ₃ C ₂ H ₅ O—C=O	1.9	13.6	5.4	L ⁴⁴
17. Polybutylmethacrylate	—CH ₂ —C— CH ₃ C ₄ H ₉ O—C=O	2.1	16.6	6.6	L ⁴⁵

Table I. (Cont'd)

Polymer	Monomer unit	$\left(\frac{h^2}{h_0^2} \right)^{1/2}$ f.r.	$A \cdot 10^8, \text{cm}$	S	Method
18. Poly-hexylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}_6\text{H}_{13}\text{O}-\text{C}=\text{O} \end{array}$	2.4	21.7	8.6	L ⁴⁶
19. Poly-octylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}_8\text{H}_{17}\text{O}-\text{C}=\text{O} \end{array}$	2.3	20.0	7.9	L ⁷⁷
20. Poly-laurylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}_{12}\text{H}_{25}\text{O}-\text{C}=\text{O} \end{array}$	2.85	30.7	12.2	L ⁷⁸
21. Polycyclohexylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}_6\text{H}_{10}-\text{C}=\text{O} \end{array}$	2.2	18.3	7.3	LA ₂ ⁷⁹
22. Poly-tert-butylphenylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ (\text{CH}_3)_3\text{C}-\text{C}_6\text{H}_4-\text{C}=\text{O} \end{array}$	2.8	29.6	11.7	LA ₂ ⁸⁰
23. Polyphenylmethacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}_6\text{H}_5-\text{C}=\text{O} \end{array}$	2.3	20.0	7.9	VA ₂ ⁸¹
24. Polycarboxyphenylmethacrylamide	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O}=\text{C}-\text{C}_6\text{H}_4-\text{N}-\text{C}=\text{O} \\ \\ \text{O}-\text{C}_2\text{H}_5 \end{array}$	2.0	25.5	10.1	VA ₂ ⁸²
25. [6,6] Nylon	—	2.1	16.6	6.6	VA ₂ ⁵⁹
26. Polydimethylsiloxane	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{O}-\text{Si}- \\ \\ \text{CH}_3 \end{array}$	1.4–1.6	14.0	4.9	V ⁸³ LA ₂ ⁸⁴
27. Polymethylphenylsiloxane	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{O}-\text{Si}- \\ \\ \text{C}_6\text{H}_5 \end{array}$	1.5	14.0	4.9	LA ₂ ⁸⁴
28. Polybutadiene	—CH ₂ —CH=CH—CH ₂ —	1.7			L ⁸⁵
29. Natural rubber (cis)	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}=\text{C} \\ \diagdown \\ \text{CH}_2 \end{array}$	1.7			V ⁸⁶
30. Gutta percha (trans)	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}=\text{C} \\ \diagup \\ \text{CH}_2 \end{array}$	1.45			V ⁸⁶
31. Ethylcellulose	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{O} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_4 \\ \\ \text{CH}_2\text{OC}_2\text{H}_5 \end{array}$	4.0	200	20	L ⁸⁷
32. Trinitrocellulose	$\begin{array}{c} \text{NO}_2 \quad \text{NO}_2 \\ \quad \\ \text{O} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_3 \\ \\ \text{CH}_2\text{ONO}_2 \end{array}$	4.2	200	20	LA ₂ ^{59, 88, 89}

dimensions $(\overline{h_0^2})^{1/2}$ to the dimensions $(\overline{h_{f.r.}^2})^{1/2}$ that the coil would have with completely free rotation of the links in the chain can serve as a measure of the thermodynamic (equilibrium) flexibility of chains in comparing the properties of polymers of different chemical structure.

Table I gives the results of determining the relative unperturbed coil dimensions $(\overline{h_0^2}/\overline{h_{f.r.}^2})^{1/2}$ for polymers of various chemical structures. Part of these results have been obtained by measuring $(\overline{h_0^2})^{1/2}$ or $[\eta]$ directly in Θ -solvents. For a number of polymers, the value of $(\overline{h^2})^{1/2}$ or $[\eta]$ was measured in good solvents. Then α , $(\overline{h_0^2})^{1/2}$, and $(\overline{h_0^2}/\overline{h_{f.r.}^2})^{1/2}$ were calculated using the measured values of M and A_2 , in line with the existing theory.^[58] It is of considerable interest to compare the flexibilities of polymer chains as the composition of the side-chain attachments is successively altered. Systematic studies along this line have been carried out with derivatives of polymethacrylic acid and polystyrene. In the former case, one can compare the flexibilities for two series, with aliphatic attachments in the side group (Nos. 15–20 in Table I), and with ring-containing attachments (Nos. 21–24). In either series, as one lengthens the side-chain attachments (makes them more complex), one notes a gradual increase in $(\overline{h_0^2}/\overline{h_{f.r.}^2})^{1/2}$ corresponding to a decrease in the flexibility of the chains.

It is pertinent here to compare the flexibility of the chains of polystyrene, poly- β -vinylnaphthalene, and the chloro-derivatives of polystyrene. The replacement of the benzene ring in the side groups of polystyrene by the naphthalene double ring leads to a considerable decrease in the thermodynamic flexibility of the chain (owing to the sharp increase in the steric hindrance of rotation of the links). However, the poly- β -vinylnaphthalene chain is still not so rigid as to affect the form of the $(Hc/I\theta)_{c=0}$ scattering curve of its solutions. The coefficient Φ for poly- β -vinylnaphthalene is anomalously small, indicating that its "optical dimensions" do not agree with its hydrodynamic dimensions. This has provided the authors of^[41] with grounds for characterizing it as a polymer having a "semirigid" chain.

A comparison of the relative unperturbed dimensions of polystyrene and its dichloro-derivatives^[40,42] permits us to draw an important conclusion on the effect of electrostatic (dipole) interactions of the side groups on the equilibrium flexibility of polymer chains. The unperturbed coil dimensions of poly-2,5-dichlorostyrene and polystyrene at an equal degree of polymerization almost coincide, while those of poly-3,4-dichlorostyrene prove to be 25% larger. The structural difference consists in the fact that when the chlorine atoms on the rings are in the 2,5-positions, the dipole moments compensate, while there is a resultant dipole moment ≈ 2.3 Debye units for the 3,4-positions in the side groups of the chain. A detailed discussion of this problem can be found in^[42].

We can draw some general conclusions on the relative thermodynamic flexibility of chain macromolecules. The most flexible ones are the polysiloxanes, and then the polymers with conjugated bonds: polybutadiene, rubber, and gutta percha. The greater flexibility of the latter as compared with the polymers of the vinyl series is apparently due to the greater freedom of rotation about the bonds adjacent to the double bonds. We might suppose that the rigidity of the chains of polyacrylonitrile involves the strong electrostatic interaction of neighboring $C \equiv N$ side groups of the chain, which have a large dipole moment (≈ 4 Debye units). Finally, the highest rigidity is shown by the macromolecules of cellulose derivatives. Thus, the composition of the main chain of a macromolecule has a greater effect on its thermodynamic flexibility than the composition of the side groups. However, in certain cases the influence of the latter is also rather high (polyvinylnaphthalene, polyacrylonitrile).

We can consider it to be established that the macromolecules of all the polymers in Table I form Gaussian coils in solution. Some exceptions are the chains of the cellulose derivatives, for which the data are contradictory. The exponent a in the Kuhn-Mark-Houwink equation

$$[\eta] = K_\eta M^a \quad (58)$$

is near unity for the cellulose derivatives. This is commonly ascribed to the partial penetrability to the solvent of its rigid (and hence open) coils. The nature of the relation of the coil dimensions $(\overline{h^2})^{1/2}$ to the molecular weight (degree of polymerization) is controversial at present. Figure 12 (from^[90]) shows the relation of the quantity $\overline{R_z^2}/M_z$ to M_z for nitrocellulose in acetone and ethyl acetate according to the data of^[88-91]. In spite of the considerable scatter of the experimental points, in the aggregate they show that the chains of nitrocellulose are rigid at small M (where $\overline{R^2}/M$ increases with M), but at $M \approx 5 \times 10^5$ they become Gaussian in behavior (where $\overline{R^2} \sim M$, and $\overline{R^2}/M$ is independent of M).

On the other hand, Meyerhoff^[92] analyzed the data

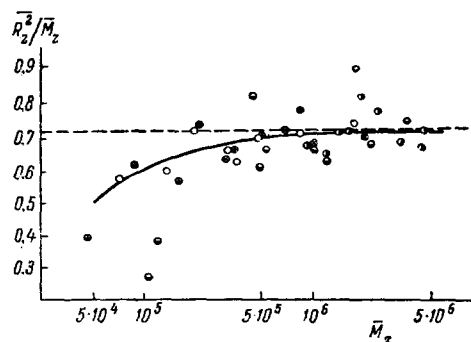


FIG. 12. The relation of the quantity $\overline{R_z^2}/M_z$ to M_z for nitrocellulose macromolecules in acetone and ethyl acetate (from the data of^[88-91]).

on the coil dimensions of nitrocellulose in acetone, and concluded that the length of the statistical segment $A = h^2/L$ increases with M more rapidly in the region of large M .^{*} This contradicts the variation in the quantity \bar{R}^2/M shown in Fig. 12. Data on the coil dimensions of cellulose tricaproate^[93] and ethylcellulose^[87] in solution indicate that the ratio \bar{R}^2/M decreases with increasing M , and approaches an asymptote (Gaussian coils, $\bar{R}^2 \sim M$) from above, rather than from below as in Fig. 12. This type of relation of \bar{R}^2 to M has not thus far received any explanation at all.

At the same time, the nature of the variation of the hydrodynamic properties of the coils with increasing molecular weight, as manifested in the variation of the coefficient Φ in the Flory-Fox relation (57), is the same for the cellulose derivatives having differing relations of \bar{R}^2 to M . For nitrocellulose in acetone^[91] and ethyl acetate,^[89] for cellulose tricaproate in 1-chloronaphthalene,^[93] and for ethylcellulose in methanol,^[87] the coefficient Φ increases with the molecular weight. A comparison of the values of $[\eta]$ and A_2 in various solvents shows in a number of cases a lack of the usual correlation between them: according to the data of^[93], the viscosity $[\eta]$ of cellulose tricaproate in a good solvent, 1-chloronaphthalene, is less than in a Θ -solvent, dimethylformamide. Contrary to the usual idea of the large dimensions of cellulose coils, the measurements of $[\eta]$ in^[94] showed that the relative unperturbed coil dimensions $(h_0^2/h_{f,r}^2)^{1/2}$ of cellulose tricaprylate and tributyrate have a value of ≈ 2.0 in certain Θ -solvents, just as for flexible polymer chains.

Such contradictions and anomalies have led certain authors^[90,95] to conclude that the specific interaction of the cellulose derivatives with certain solvents (especially the polar ones) can have a prevailing influence on the height of the potential barriers limiting the freedom of rotation of the links in the chain. Thus it governs the coil dimensions and the value of $[\eta]$. Thus, further study is required to determine the true properties of the molecules of the cellulose derivatives in solution. These studies are also of current interest as a necessary stage in understanding the true properties and structures of other rigid polymers. in particular DNA.

6. THE STUDY OF POLYDISPERSITY

Up to now, we have assumed that the particles in solution are identical both in shape and in mass (M). However, in polymer solutions the latter condition is practically never completely obeyed, and the assemblage of particles is characterized by some mass distribution. As Zimm^[29] showed, the nature of this dis-

tribution directly affects the angular dependence of the light scattering of the solutions, while the measured values of M and $(\bar{R}^2)^{1/2}$ are averages. An essential point here is that the mean M and $(\bar{R}^2)^{1/2}$ obtained by the light-scattering method involve different types of averaging.

To elucidate the physical reasons for the differing type of averaging for the molecular weight and the particle dimensions, we shall consider the general equation for the scattering intensity (10), writing it as follows:

$$\frac{I_{0v}}{c} = HMP_v(\theta). \quad (59)$$

Now we shall assume that the polymer is polydisperse, and that its dispersion is characterized by a normalized distribution function $f(N)$, so that $f(N)dN$ is the weight fraction of the particles having a degree of polymerization N lying in the range from N to $N+dN$. At "infinite dilution" the total scattering of the solution is the sum of the scattering intensities of the individual particles. Then,

$$\left(\frac{I_{0v}}{c}\right)_{c=0} = H \int Mf(N)P_v(\theta) dN, \quad (60)$$

where the integration is performed over all possible N . For small scattering angles, according to (46), we can write

$$\left(\frac{I_{0v}}{c}\right)_{c=0} = H \int Mf(N) \left[1 - \frac{1}{3}\bar{R}^2\mu^2\right] dN. \quad (61)$$

If the particles being studied are random Gaussian coils, for which^[8] $\bar{R}^2 = KM = KNM_0$ (where M_0 is the weight of the monomer unit), then

$$\left(\frac{I_{0v}}{c}\right)_{c=0} = HM_0 \int Nf(N) dN - \frac{1}{3}HKM_0^2\mu^2 \int N^2f(N) dN. \quad (62)$$

Using the function $f(N)$, the different types of averages of the degree of polymerization are defined as follows:^[8]

number-average

$$N_n = \left[\int \frac{Nf(N)}{N} dN \right]^{-1}, \quad (63)$$

weight-average

$$N_w = \int Nf(N) dN, \quad (64)$$

and z-average

$$N_z = \frac{1}{N_w} \int N^2f(N) dN. \quad (65)$$

Correspondingly, the molecular weights are:

$$M_n = M_0N_n, \quad M_w = M_0N_w \quad \text{and} \quad M_z = M_0N_z.$$

Thus,

$$\left(\frac{Hc}{I_{0v}}\right)_{c=0} = \frac{1}{M_w} \left(1 + \frac{1}{3}K\mu^2M_z\right). \quad (66)$$

Equation (66) implies that the intercept of the graph of Hc/I_{0v} plotted against $\sin^2(\theta/2)$ (or against μ^2 ,

*See the footnote following Eq. (33).

which is the same thing) is a quantity inversely proportional to the weight-average molecular weight M_W . However, the initial slope of the graph is determined by the coil dimensions $\bar{R}_Z^2 = KM_Z$, which corresponds to the z-average molecular weight. We see from examining Eq. (66) that the scattering phenomenon in a polydisperse solution occurs in such a way that the "forward scattering" ($\theta = 0$), which determines the measured value of the molecular weight M_W corresponds to the averaging of the first power of the molecular weight (the first term). However, the decline in the scattering with increase in the angle θ , which determines the measured value of the coil dimensions \bar{R}_Z^2 , corresponds to the averaging of the square of M (the second term).

Zimm^[29] was also the first to establish the asymptotic behavior of the function $P_V^{-1}(\theta)$ for large values of the argument (for both coils and rods). He pointed out that the form of the graph of the function $P_V^{-1}(\theta)$ plotted against $\sin^2(\theta/2)$ depends on the type of polydispersity.

A very simple estimate of the polydispersity is based on comparing the average molecular weights M_n , M_w , and M_z of a sample; M_w is determined by light scattering. M_n and M_z can be determined by the methods of osmometry and sedimentation equilibrium. The study of polydispersity within the limits of the light-scattering method alone requires measurements of the angular dependence of the scattering of the solutions.

After Zimm,^[29] the problem of the effect of polydispersity on the scattering indicatrix of polymer solutions was studied in detail by Benoit.^[96] Polydispersity affects the asymptotic behavior of the function $P_V^{-1}(\theta)$. As has been shown in^[29,96], the variation of the function $P_V^{-1}(\theta)$ at large values of the argument x is described by the equation

$$P_{v\infty}^{-1}(\theta) = \frac{1}{2} \frac{M_w}{M_n} + \frac{x_w}{2} \quad (67)$$

(here x_w indicates that the weight-average value of the coil dimensions \bar{R}_W^2 is used in Eq. (33) for x). For the intercept A_∞ of the asymptote $P_V^{-1}(\theta)$, this gives

$$\frac{A_\infty}{A_0} = \frac{1}{2} \frac{M_w}{M_n}$$

and, taking into account the fact that $A_0 = 1/M_w$,

$$A_\infty = \frac{1}{2M_n}. \quad (68)$$

The equation of the function $P_V^{-1}(\theta)$ for small x is

$$P_V^{-1}(\theta) = 1 + \frac{x_z}{3}. \quad (69)$$

From (67) and (69), we can derive the following expression for the ratio of slopes of the asymptote s_∞ and the initial tangent s_0 of the graph of the function $P_V^{-1}(\theta)$ or the curve $(Hc/I_{\theta V})_{c=0}$:

$$\frac{s_\infty}{s_0} = \frac{3}{2} \frac{x_w}{x_z} = \frac{3}{2} \frac{M_w}{M_z}. \quad (70)$$

Since in any case $M_w \leq M_z$, polydispersity diminishes the slope of the asymptote, and $s_\infty/s_0 \leq 3/2$. In the special case where the sample has a distribution for which $M_z:M_w:M_n = 3:2:1$, the ratio s_∞/s_0 is unity, and the curve for $(Hc/I_{\theta V})_{c=0}$ degenerates into a straight line.^[29] According to (67), we can also derive

$$\frac{s_\infty}{A_\infty} = \frac{1}{2} \left(\frac{8\pi^2}{3} \frac{\bar{R}_w^2}{\lambda^2} \right) : \frac{1}{2} \frac{M_w}{M_n} = \frac{8\pi^2}{3} \frac{\bar{R}_w^2}{\lambda^2},$$

whence

$$\frac{\bar{R}_w^2}{\lambda^2} = \frac{3}{8\pi^2} \frac{s_\infty}{A_\infty}. \quad (71)$$

Thus, by studying the properties of the scattering indicatrix, we can determine M_n , M_w , and M_z and the corresponding average dimensions for a polydisperse system of Gaussian coils (Fig. 13).

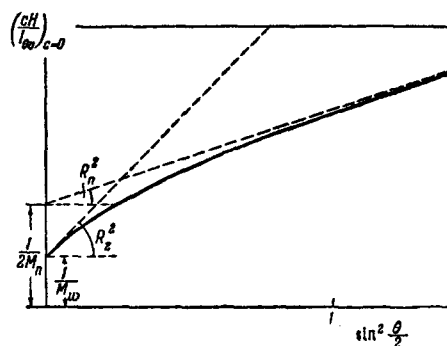


FIG. 13. Determination of the mean square radius of gyration \bar{R}^2 of the coils and the molecular weight M from the graph of $(Hc/I_{\theta V})_{c=0}$ plotted against $\sin^2(\theta/2)$ for a polydisperse sample

The theoretical relations presented above have been used in a number of studies.^[97,98] In^[99], they were tested on samples having a given polydispersity (as obtained by mixing narrow fractions of polystyrene in definite proportions). The agreement of the calculated and measured values of M_w and M_z was quite satisfactory. We note that the agreement was considerably poorer for M_n (this has also been noted in^[98]).

Apparently the reason for this lies in the difficulties of extrapolating the asymptote of the $(Hc/I_{\theta V})_{c=0}$ curve to determine its intercept.

The influence of polydispersity on the light scattering of solutions of rodlike particles has been discussed in^[100], which showed that the asymptote of the curve of $(Hc/I_{\theta V})_{c=0}$ plotted against $\sin(\theta/2)$ (instead of $\sin^2(\theta/2)$ as for coils) permits one to obtain

$$\left. \begin{aligned} M_n &= \frac{2}{\pi^2 A_\infty} \\ L_n &= \frac{1}{2\pi^2} \frac{s_\infty}{A_\infty} \end{aligned} \right\} \quad (72)$$

and

In conjunction with M_w and \bar{R}_{Z+1}^2 , which can be deter-

mined from the ordinary double-extrapolation curves of (Hc/I_{θ_V}) against $\sin^2(\theta/2)$, Eqs. (72) give sufficient information on the polydispersity. A more complex case has been discussed in ^[101] involving light scattering in a system of rodlike particles that are polydisperse both in length and thickness.

We must bear in mind that one can draw quantitative conclusions on the polydispersity from the form of the $(Hc/I_{\theta_V})_{c=0}$ curve when all other factors affecting the variation of the function $P_V^{-1}(\theta)$ have been eliminated: branching or rigidity of the chains, or volume effects (see below). For ordinary (flexible) unbranched polymers, one must therefore measure the polydispersity in poor solvents, especially at high molecular weights.

We should point out that a number of authors ^[102-106] have suggested estimating the polydispersity of samples from the value of the second virial coefficient A_2 of their solutions.

7. THE STUDY OF BRANCHING IN CHAIN MACROMOLECULES

As is known, branching leads to a considerable decrease in the mean coil dimensions $(\bar{R}^2)^{1/2}$ as compared with the dimensions of linear macromolecules at the same degree of polymerization. ^[107,108] The greater degree of swelling of branched macromolecules only slightly obscures this phenomenon. ^[109]

The study of branching can be based in principle on comparing \bar{R}^2/M for linear and branched samples of a given polymer. Here the decrease in the ratio \bar{R}^2/M serves as a measure of the branching. A number of authors have studied in this way the branching of polystyrene ^[110,111] and polyethylene. ^[112,113] However, this method involves an essential difficulty arising from the great polydispersity of the branched samples. Since the light-scattering method gives different types of averages for the quantities \bar{R}^2 and M , we must make a correction for polydispersity. This correction is never accurate enough for a sound comparison of \bar{R}^2/M of branched and linear samples.

Hence, it is more reliable to estimate the branching from the value of $[\eta]$ (and determine M by the light-scattering method). A certain degree of polydispersity in the samples does not displace the points on the graph of $\log[\eta]$ against $\log M$, owing to the similarity in the type of average made in the viscosity and light-scattering measurements (especially in good solvents). A given degree of branching leads to a corresponding downward shift in the point from the straight line on this graph, as Thurmond and Zimm ^[114] showed with model branched copolymers (Fig. 14). Following ^[114], such a method has become rather widely used. In particular, in ^[115] they measured the intrinsic viscosity and light scattering of linear polystyrene and a styrene-styrene graft polymer. They showed that $[\eta]$, $(\bar{R}^2)^{1/2}$, and A_2 for the branched samples (the graft

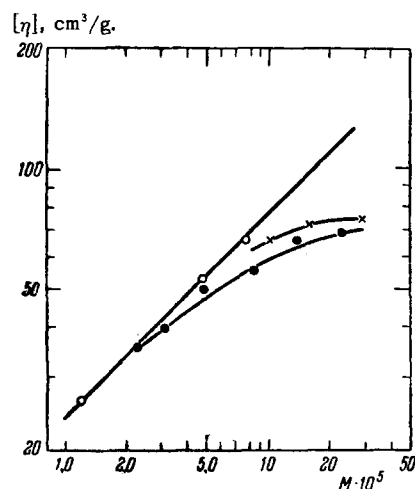


FIG. 14. Graph of the intrinsic viscosity $[\eta]$ as a function of the molecular weight for linear (open circles) and branched (solid circles and crosses) polystyrene fractions in butanone-propanol mixture. ^[114] Scale: logarithmic. The slope of the straight line corresponds to $[\eta] \sim M^{0.5}$.

polymer) were lower than for a linear polymer of the same molecular weight. The coefficient Φ in the Flory-Fox relation (57) proved to be appreciably higher for the branched samples than for the linear ones.

Meyerhoff and Cantow ^[116] came to the conclusion that the ordinarily-used samples of "linear" polystyrene actually are always somewhat branched (of the order of one branch per $(3-4) \times 10^3$ monomer units of the chain). We should note two more of the results obtained in ^[116]. Along with the general increase in branching (as characterized by the decrease in \bar{R}^2/M) with increasing molecular weight, the ratio of the number of branches per molecule to M decreases with increasing M . This involves the fact that the branched structure of the macromolecules becomes more "uniform" with increasing M (less frequent, but longer branches). The macromolecules of isotactic polystyrene, in distinction from the atactic material, proved to be not branched at all.

As was recently ascertained, all the quantitative estimates of branching from the value of the intrinsic viscosity $[\eta]$ in studies prior to 1959 require serious corrections. It had been assumed ^[32] that Eq. (57) is valid even for branched chains, and hence,

$$\frac{[\eta]_g}{[\eta]_l} \sim \frac{(\bar{R}^2)_g^{3/2}}{(\bar{R}^2)_l^{3/2}},$$

where the subscripts g and l refer to branched and linear samples of the same molecular weight. Zimm and Kilb ^[117] examined the hydrodynamic interaction of the links in a branched chain, and showed that $[\eta]_g/[\eta]_l$ is proportional to the ratio $(\bar{R}^2)_g^{1/2}/(\bar{R}^2)_l^{1/2}$, rather than $(\bar{R}^2)_g^{3/2}/(\bar{R}^2)_l^{3/2}$, as had been previously assumed. According to Bueche, ^[118] the physical meaning of this law is that the hydrodynamic dimen-

sions of branched coils are determined not by the mean radius of gyration $(\overline{R^2})^{1/2}$, but by the distance from the center of the coil at which the density of segments (links) attains a certain value.

A further treatment of this problem is found in [119, 120]. In particular, it was shown in [119] that in the presence of polydispersity, one cannot get data on the degree of branching (grafting) of macromolecules by comparing the dimensions $(\overline{R^2})^{1/2}$ and $(\overline{R^2})_l^{1/2}$ at equal values of M_w (in view of the fact that $\overline{R^2}$ and M are determined by light scattering). They can be obtained by comparing the intrinsic viscosities $[\eta]_g$ and $[\eta]_l$ (at equal M_w). This situation is illustrated by Fig. 15, taken from [119], which shows the values of $(\overline{R^2})_g/(\overline{R^2})_l$ and $[\eta]_g/[\eta]_l$ (for equal M_n , M_w , and M_z , respectively) for different branching factors γ (from $\gamma = 0$ for a linear polymer to $\gamma = 1$ at the onset of gel formation).

Benoit [121] has examined in general form the effect of branching on the angular distribution of the scattered light. He showed that this effect must consist in a variation in the ratio s_∞/s_0 of the $(Hc/I_{\theta V})_{c=0}$ graph, such that

$$\left(\frac{s_\infty}{s_0}\right)_g = \frac{3}{2} \frac{\overline{R_l^2}}{\overline{R_g^2}} \quad (73)$$

Since $\overline{R_g^2} < \overline{R_l^2}$, then $(s_\infty/s_0)_g > 3/2$, and branching must distort the scattering indicatrix in a direction opposite to the effect of polydispersity. In [121], an equation is derived for the asymptote of the graph of the function $P_V^{-1}(\theta)$ for a solution of branched macromolecules. In the simplest case of branched macromolecules that are monodisperse in mass, the equation of the asymptote has the form

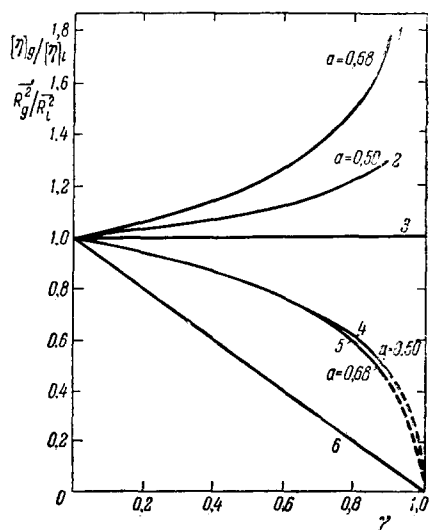


FIG. 15. The relation of the ratio of viscosities $[\eta]_g/[\eta]_l$ (curves 1, 2, 4, and 5) and of the mean square radii of gyration $\overline{R}_g^2/\overline{R}_l^2$ (straight lines 3, 6) for branched and unbranched macromolecules of the same molecular weight: M_n (1, 2), M_w (3, 4, 5) and M_z (6) [119] [a is the exponent in Eq. (58)].

$$P_{\infty}^{-1}(\theta) = \frac{1}{2} + \frac{x}{2} - \sum_m \frac{(m-1)(m-2)}{4} z_m, \quad (74)$$

where z_m is the number of branch points of functionality m in the macromolecule.* The third term in the equation is characteristic of branched chains. If the functionality m of all branch points in the molecule were the same, then in principle we could determine the number of branches from the intercept of the asymptote. In the case nearer to practice, having polydispersity both in mass and degree of branching, the equation of the asymptote is more complex, and includes the mass distribution function of the particles. It becomes possible to determine the branching parameters from the asymptote of the $(Hc/I_{\theta V})_{c=0}$ curve when the branches are all of the same functionality m throughout the macromolecule, or when the mass polydispersity (the ratio M_w/M_n) has been determined by another independent method.

Now, the slope s_∞ of the asymptote of the $P_V^{-1}(\theta)$ curve is determined by the weight-average coil dimensions [Eq. (67)], while its initial slope s_0 is determined by the z -average dimensions [Eq. (69)]. Thus, when branching and polydispersity are simultaneously present, according to (73), (67), and (69),

$$\frac{s_0}{s_\infty} = \frac{2}{3} \frac{\langle \overline{R}_g^2 \rangle_z}{\langle \overline{R}_l^2 \rangle_w} \quad (75)$$

Taking into account the fact that $\langle \overline{R}_l^2 \rangle_z / \langle \overline{R}_l^2 \rangle_w = M_z/M_w$, we obtain from (75)

$$\frac{s_0}{s_\infty} = \frac{2}{3} \frac{M_z}{M_w} \frac{\langle \overline{R}_g^2 \rangle_z}{\langle \overline{R}_l^2 \rangle_z} \quad (76)$$

Equation (76) implies that we cannot distinguish the effects of polydispersity and branching in the initial and asymptotic slopes of the light-scattering indicatrix, and (in agreement with Kilb [119]), we must supply additional data. These might be data on the polydispersity (M_z/M_w) obtained from sedimentation; here we could determine a measure of the branching

$$g_z = \frac{\langle \overline{R}_g^2 \rangle_z}{\langle \overline{R}_l^2 \rangle_z}$$

or else, intrinsic-viscosity data. In the latter case, according to [119], we can determine the following quantity from the ratio $[\eta]_g/[\eta]_l$ (at equal M_w):

$$g_z = \frac{\langle \overline{R}_g^2 \rangle_z}{\langle \overline{R}_l^2 \rangle_z} = 1 - \gamma \quad (77)$$

In such a case, the polydispersity can be calculated by substituting (77) into (76):

$$\frac{M_z}{M_w} = \frac{3}{2} \frac{s_0}{s_\infty} \frac{1}{1-\gamma} \quad (78)$$

The determination of the degree of branching from the ratio s_0/s_∞ is very rarely applied in practice,

*The functionality of a branch point means the number of branches arising at the given point.

since here one must completely exclude all other factors affecting the form of the scattering indicatrix: polydispersity, volume effects (which are especially marked for branched molecules), etc. As a rather rare example of determining branching from the form of the $(Hc/I_{\theta_V})_{c=0}$ curve, we can refer to [122], in which a highly branched native dextran was studied.

An attempt has been made to use the value of the second virial coefficient of solutions to estimate branching. [123]

8. THE SCATTERING INDICATRIX AND VOLUME EFFECTS IN POLYMER CHAINS

It has been shown experimentally in [99] that the scattering indicatrix [the graph of the relation of $(Hx/I_{\theta_V})_{c=0}$ to $\sin^2(\theta/2)$] for a given polymer fraction changes in form as we go from a poor to a good solvent. This problem has been treated theoretically by O. B. Ptitsyn, [124] and later by Benoit [125] and by Hyde et al., [126] as well as other authors. [127] According to the cited studies, the scattering indicatrix corresponds in an ideal solvent to the Debye scattering function $P_V^{-1}(\theta)$, but changes in good solvents, owing to the distortion of the Gaussian structure of the coils. The reason for this distortion lies in the "volume effects," the repulsion of links of the polymer coil in fortuitous proximity and their interaction with molecules of the solvent.

The abovementioned theories [124-126] are based on the assumption that the mean square \bar{r}_{pt}^2 of the distance between a pair of links p and t in the chain increases faster than proportionally to the number of links $|t-p|$ between them; in particular,

$$\bar{r}_{pt}^2 \sim |t-p|^{1+\epsilon},$$

where ϵ is the parameter entering into Eq. (56). At the same time, the distribution function of the links (segments) in the chain is assumed to be Gaussian as before. Naturally, since these theories proceed from identical assumptions, they lead to coincident results. These results are represented in the form of a certain scattering function $P_V(\theta, \epsilon)$ in the studies of O. B. Ptitsyn and Benoit, which has been tabulated in the paper by Hyde et al. The function $P_V(\theta, \epsilon)$ taking into account the volume effects has the form [124]

$$P_V(\theta, \epsilon) = \frac{2}{1+\epsilon} \left\{ \kappa^{-\frac{1}{1+\epsilon}} \left(-\frac{\epsilon}{1+\epsilon}, \kappa \right)! - \kappa^{-\frac{2}{1+\epsilon}} \left(\frac{1-\epsilon}{1+\epsilon}, \kappa \right)! \right\}, \quad (79)$$

where

$$\kappa = x \left(1 + \frac{5\epsilon}{6} + \frac{\epsilon^2}{6} \right),$$

and x is the argument of the Debye scattering function $P_V(\theta)$ defined by Eq. (33), and

$$(q, \kappa)! = \int_0^{\kappa} e^{-\tau} \tau^q d\tau$$

is the incomplete Γ -function.

Figure 16 shows the variation of the scattering function $P_V^{-1}(\theta, \epsilon)$ as a function of x for various values of the parameter ϵ within the range from 0.05 to 0.30. The curve $\epsilon = 0$ corresponds to the Debye scattering function $P_V^{-1}(\theta)$, since $P_V(\theta, 0) \equiv P_V(\theta)$. We see also from Fig. 16 that the influence of the volume effects brings about a decrease in the asymptotic slope of the $P_V^{-1}(\theta, \epsilon)$ curve at large x , as compared with the behavior of the function $P_V^{-1}(\theta)$, similar to the effect of polydispersity. Precisely this sort of deformation of the scattering indicatrix has been observed experimentally. [99] The value of the ratio s_0/s_∞ of the initial and asymptotic slopes of the function $P_V^{-1}(\theta, \epsilon)$ as a function of $(h^2/\lambda^2)^{1/2}$ and ϵ has been calculated by O. B. Ptitsyn. [124] We shall give here only the expression for $P_{V\infty}^{-1}(\theta, \epsilon)$ in the region of large values of the argument x :

$$P_{V\infty}^{-1}(\theta, \epsilon) = \frac{\kappa^{\frac{1}{1+\epsilon}}}{2\Gamma\left(1 + \frac{1}{1+\epsilon}\right) - \frac{\Gamma\left(1 + \frac{2}{1+\epsilon}\right)}{\kappa^{\frac{1}{1+\epsilon}}}}, \quad (80)$$

or

$$P_{V\infty}^{-1}(\theta, \epsilon) = \frac{1+\epsilon}{2} \frac{\left(1 + \frac{5\epsilon}{6} + \frac{\epsilon^2}{6}\right)^{\frac{1}{1+\epsilon}} \kappa^{\frac{1}{1+\epsilon}}}{\Gamma\left(\frac{1}{1+\epsilon}\right)} + \frac{1+\epsilon}{2} \frac{\Gamma\left(\frac{2}{1+\epsilon}\right)}{\Gamma^2\left(\frac{1}{1+\epsilon}\right)}. \quad (80a)$$

It was found from these studies that the unreserved use of the dissymmetry method, ignoring the actual form of the angular dependence of the scattering, is inadmissible in good solvents and in studying samples of very high molecular weight. It is essential to take

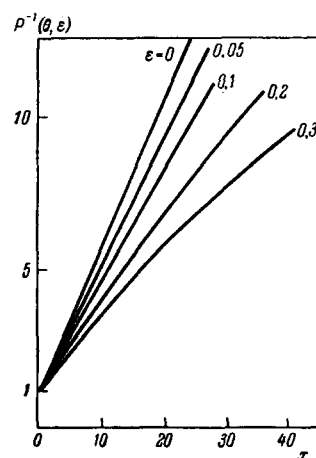


FIG. 16. The relation of the function $P_V^{-1}(\theta, \epsilon)$ to the argument $x = 16\pi^2 \cdot (\bar{R}^2/\lambda^2) \sin^2(\theta/2)$ for various values of the parameter ϵ . [124]

into account the deformation of the scattering indicatrix, not only in obtaining the true values of M and $(R^2)^{1/2}$, but also in determining polydispersity correctly by the light-scattering method. We recall that the polydispersity data are obtained from the deviation of the measured slope ratio s_0/s_∞ from the value $2/3$. Loucheux, Weill, and Benoit^[128] have shown that in principle one can obtain polydispersity data in good solvents; they found that the asymptotic behavior of the function $P_V^{-1}(\theta, \epsilon)$ in the region of large values of x does not change in the presence of polydispersity. The interpretation of the results of the measurements is rather complex in this case. Put very briefly, it amounts to the following procedure. Since according to (80a), $P_V^{-1}(\theta, \epsilon)$ is a linear function of $[\sin^2(\theta/2)]^{1/(1+\epsilon)}$, the authors^[128] find ϵ from the slope of the graph of $\log(1/I_{\theta V})$ plotted against $\log \sin^2(\theta/2)$. The molecular weight and the coil dimensions are then determined by constructing a plot of $(Hc/I_{\theta V})_{c=0}$ against $[\sin^2(\theta/2)]^{1/(1+\epsilon)}$ and an ordinary double-extrapolation graph (Zimm plot) of $(Hc/I_{\theta V})$ against $[\sin^2(\theta/2) + kc]$. One takes the intercept and the slope of the asymptote from the first graph, and the initial slope and intercept of the curve from the second graph. Thorough experimental study shows that, while the scattering indicatrix of a polymer in a good solvent deviates from the Debye function $P_V^{-1}(\theta)$, at the same time it does not precisely agree with the function $P_V^{-1}(\theta, \epsilon)$. Such a study has been made in^[129] with a very narrow ("monodisperse") polystyrene fraction ($M = 20 \times 10^6$) in an ideal solvent (cyclohexane) and a good solvent (toluene) (Fig. 17). The determination of the coil dimensions in toluene from the intrinsic dissymmetry $|z|$, using the function $P_V^{-1}(\theta)$, gave $(\bar{h}^2)^{1/2} = 5000 \text{ \AA}$ and $\alpha = 2.0$. The following method was used to calculate $(\bar{h}^2)^{1/2}$ using the function $P_V^{-1}(\theta, \epsilon)$. The ratio $P_V^{-1}(\theta, \epsilon)/P_V^{-1}(\theta)$ was calculated as a function of α for several values of the swelling coefficient near $\alpha = 2.0$. Then the value of α for which the function $P_V^{-1}(\theta, \epsilon)$ best approximated the experimental points was found by the least-squares method. This value proved to be $\alpha = 2.4$, cor-

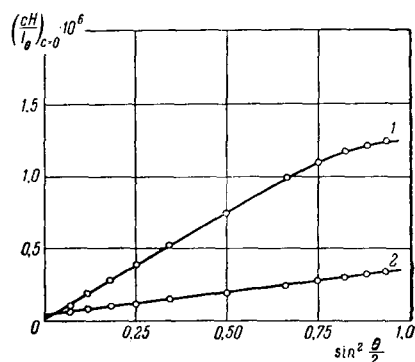


FIG. 17. The form of the curve of the quantity $(Hc/I_{\theta V})_{c=0}$ as a function of $\sin^2(\theta/2)$ for a polystyrene fraction having $M = 20 \times 10^6$ in toluene (1) and in cyclohexane (2).^[129]

responding to coil dimensions $(\bar{h}^2)^{1/2} = 6000 \text{ \AA}$.

Thus, the difference in the coil dimensions of a polystyrene of very high molecular weight in toluene, as calculated with account taken of the influence of volume effects, and without, amounted to 20%. The difference is quite substantial, but considerably less than we should expect on the basis of the theoretical function $P_V^{-1}(\theta, \epsilon)$ (for a given $(\bar{h}^2/\lambda^2)^{1/2}$).^[126] An analogous method of determining the dimensions $(\bar{h}^2)^{1/2}$ using the function $P_V^{-1}(\theta, \epsilon)$ has been applied in^[38] to a series of high-molecular-weight fractions of poly-2,5-dichlorostyrene in dioxane.

We should note that the points on the graphs of $\log(1/I_{\theta V})$ against $\log \sin^2(\theta/2)$ do not in all cases fit a straight line.^[129,38] This is a manifestation of the fact that the measured scattering indicatrix does not exactly correspond to the variation of the theoretical function $P_V^{-1}(\theta, \epsilon)$. This can be illustrated by Fig. 18, which shows the ratio $P_V^{-1}(\theta, \epsilon)/P_V^{-1}(\theta)$ plotted against $\sin^2(\theta/2)$ for polystyrene fractions ($M = 20 \times 10^6$) in toluene and cyclohexane. The circles correspond to the measured scattering intensities, while the curve is calculated from the theoretical functions $P_V^{-1}(\theta, \epsilon)$ and $P_V^{-1}(\theta)$. It seems to us that the observed discrepancy could arise from employing a single parameter ϵ in the theory in taking into account the influence of volume effects on the relative distances of both distant (along the chain) and close pairs of chain elements. Thus, the description of the phenomenon with a single parameter ϵ must apparently involve a certain distortion. This problem requires further theoretical treatment. It would also be desirable to perform additional thorough experiments, since the existing experimental material is still greatly limited.

Leng and Benoit^[130] have used the light-scattering method for a direct experimental proof of the influence of volume effects on the dimensions of polymer coils in solution. These authors used a block polymer of the type ABA, in which short chains A of polymethylmethacrylate (PMMA) (amounting to from 7 to 40% of the block polymer) had been joined to the ends of

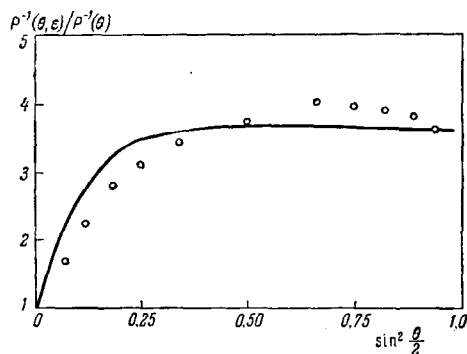


FIG. 18. The ratio of the quantities $P_V^{-1}(\theta, \epsilon)$ and $P_V^{-1}(\theta)$ as a function of $\sin^2(\theta/2)$. Curve — theory,^[124-126] circles — experiment.^[129]

long polystyrene (PS) chains B of molecular weight from 3×10^5 to 1×10^6 . The double-extrapolation method was used to measure the radius of gyration $(\overline{R^2})^{1/2}$ of the coils of the original PS samples and the block polymer in benzene, which is a good solvent for both components of the block polymer. This solvent was chosen with the intent of using the highly effective method of "phantoms" in light scattering. In fact, since the increment dn/dc of PMMA in benzene is near zero, the blocks of this polymer will contribute nothing to the scattering intensity of the block polymers in benzene. Thus, they could compare the dimensions of PS coils in benzene with the dimensions of the same coils when blocks of PMMA had been attached to the ends, increasing the volume effects for the coils of the block polymers. Multiply-repeated experiments showed (with an error no greater than 4%) that in all cases the $(\overline{R^2})^{1/2}$ of the PS coils in the block polymers is increased by 12–15% with respect to the coil dimensions of the original PS.

9. THE STUDY OF MACROMOLECULES HAVING RIGID CHAINS

The fact that the scattering indicatrix of the solutions of certain chain polymer molecules, in particular deoxyribonucleic acid (DNA), does not agree with the Debye scattering function $P_V^{-1}(\theta)$ ^[131] has made it necessary to examine the problem of scattering in solutions of particles more rigid than the Gaussian coils. Thus, A. Peterlin^[132,133] has calculated the scattering function $P(\theta)$ for wormlike chain molecules of varying rigidities (persistence length^[134] a)

The scattering function $P(\theta)$ for wormlike chains has also been discussed by Benoit and Doty^[135] and by Hermans et al.^[136,137] In the latter reference, they also studied the scattering from solutions of zigzag chains.

We should note that the application of the light-scattering method to study native DNA molecules encounters certain difficulties involving the large dimensions of these macromolecules. The latter fact makes it impossible to obtain a true initial slope of the $(Hc/I_{\theta V})_{c=0}$ curve at the smallest scattering angles θ (25–30°) attainable with the existing experimental technique. In line with this, as Sadron^[138] has emphasized, the data obtained by the light-scattering method on the molecular weights and (especially) the dimensions of DNA molecules cannot be considered to be sufficiently precise. Sadron pointed out^[138,139] that the asymptotic branch of the graph of $(Hc/I_{\theta V})_{c=0}$ as a function of $\sin(\theta/2)$ for DNA solutions is linear. Theoretically, this corresponds to the case of rodlike particles (in distinction from Gaussian coils). However, the asymptote intersects the vertical axis at a negative intercept, while for rodlike particles it is positive. In Sadron's opinion, relying on the calculations of Luzzati and Benoit,^[140] this type of relation

of $(Hc/I_{\theta V})_{c=0}$ to $\sin(\theta/2)$ is evidence of a zigzag structure of native DNA molecules. Luzzati and Benoit showed that the following relation holds for the asymptote of the scattering curve of solutions of particles consisting of N linear freely-linked segments, each of length l :

$$\left(\frac{Hc}{I_{\theta V}}\right)_{c=0} = A \sin \theta/2 + B = \frac{4}{\lambda} \frac{Nl}{M} \sin \theta/2 + \frac{N}{\pi^2 M} \left(2 - \frac{\pi^2}{2} \frac{N-1}{N}\right). \quad (81)$$

The distinction from a Gaussian freely-linked chain consists in the fact that in this case l cannot be considered to be much smaller than λ . When $N = 1$, Eq. (81) goes over into the well-known formula for the asymptote of the scattering curve of rodlike particles^[100]

$$\left(\frac{Hc}{I_{\theta V}}\right)_{c=0} = \frac{4}{\lambda} \frac{L}{M} \sin \frac{\theta}{2} + \frac{2}{\pi^2 M}. \quad (82)$$

Evidently, when $N \geq 2$, the second term of Eq. (81) is negative.

Recently Ptitsyn and Fedorov^[141] have shown that the zigzag model of a macromolecule is not the only one giving rise to a negative intercept of the asymptote of the $(Hc/I_{\theta V})_{c=0}$. As these authors showed, for solutions of wormlike molecules whose rigidity is characterized by the value of the persistence length a , the second term B of Eq. (81) for the asymptote of the scattering curve $(Hc/I_{\theta V})_{c=0}$ takes on the form

$$B = \frac{2}{\pi^2 M_n} - \frac{2}{3\pi^2 m a}, \quad (83)$$

where $m = M/L$ is the mass (in molecular-weight units) per unit length of the particle, whose total length is L . For DNA molecules, $L \gg a$, and hence, $B < 0$. The first term A for solutions of wormlike chains is $(4/\lambda m) \sin(\theta/2)$, coinciding with the corresponding term in Eq. (81), considering that $Nl = L$, and $Nl/M = m^{-1}$. Ptitsyn and Fedorov thus showed that a negative intercept of the asymptote of the graph of $(Hc/I_{\theta V})_{c=0}$ against $\sin(\theta/2)$ does not solve the problem of whether a zigzag or wormlike model is preferred for the DNA molecule. For either model, one can determine a quantity $m = M/L$ from the asymptotic slope. Since for native DNA molecules the first term in (83) is much smaller than the second, one can also calculate the persistence length a of the chain from the intercept of the asymptote. The problem of interpreting the light-scattering data from DNA solutions has been subjected to further discussion in^[142], where it was noted that for Gaussian coils of sufficiently large dimensions it is very hard to establish experimentally the true nature of the relation of the function $P_V^{-1}(\theta)$ to the angle θ in its asymptotic portion. Plotting $(Hc/I_{\theta V})_{c=0}$ for solutions of large Gaussian coils as a function of $\sin(\theta/2)$, one can obtain a straight line with a negative intercept for points

at $\theta \geq 90^\circ$ (even with a scatter in the experimental points that is not too great). It is especially easy to obtain the asymptotic branch of the $(Hc/I_{\theta V})_{c=0} \sim \sin(\theta/2)$ curve for solutions of polydisperse coils.

Thus, one can get a negative intercept of the asymptotic line of the $(Hc/I_{\theta V})_{c=0} \sim \sin(\theta/2)$ curve either for zigzag or wormlike molecules, or even for large enough Gaussian coils (especially polydisperse ones, whereas DNA samples are evidently polydisperse^[138]).

The slope of the asymptotic line can give more definite indications: the value $m = M/L$ obtained from the slope can be compared with the data obtained by other methods.

In^[142], the light scattering of solutions of native DNA from calf thymus was measured. The molecular weight M_w was found from double-extrapolation graphs (Zimm plots), and in two experiments turned out to be 16.6×10^6 and 14.3×10^6 . One of the graphs is shown in Fig. 19. The value of $m = M/L$ was determined from the slope of the asymptotic lines of the graphs of $(Hc/I_{\theta V})_{c=0}$ as a function of $\sin(\theta/2)$ (Fig. 20). The values turned out to be 240 and 290 \AA^{-1} , respectively. These values of m agree with $m = 200 \text{ \AA}^{-1}$ for the well-known Crick-Watson model. From the intercept of the asymptote B, the persistence length a was calculated. In the two experiments, this turned out to be 180 and 200 \AA . The experimental data of other authors, discussed in^[141], give $a \approx 220\text{--}320 \text{ \AA}$. The value $a \approx 200\text{--}300 \text{ \AA}$ agrees with the estimate ($\sim 360 \text{ \AA}$) made on the basis of sedimentation data.

Sadron^[139] had earlier obtained a similar value $m \approx 220\text{--}250 \text{ \AA}$ by interpreting his data on the basis

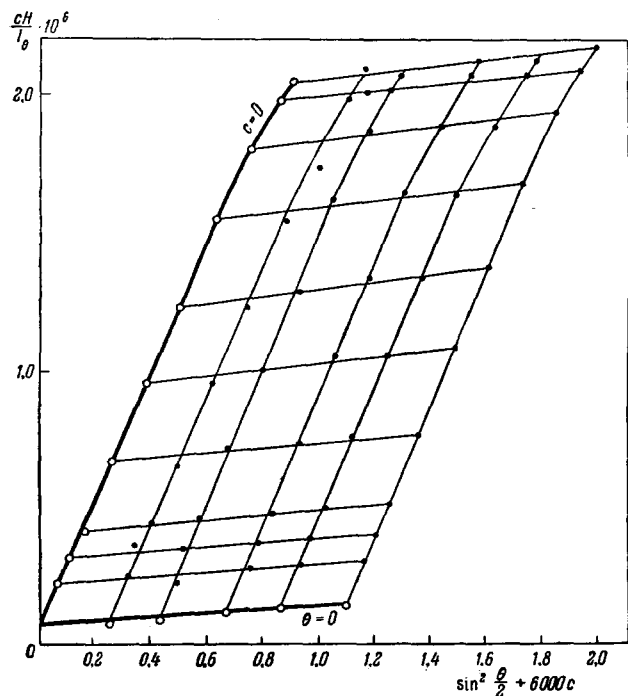


FIG. 19. Zimm plot of the light scattering of solutions of calf thymus DNA, $M_w = 15.5 \times 10^6$.^[142]

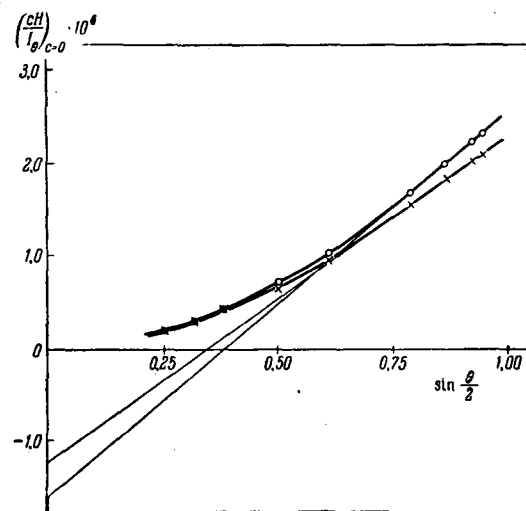


FIG. 20. Graph of the relation of $(Hc/I_{\theta})_{c=0}$ to $\sin(\theta/2)$ for solutions of calf thymus DNA.^[142] The straight lines are the asymptotes of the curves.

of a zigzag chain model. Figure 21 shows the graph of the relation of $(Hc/I_{\theta V})_{c=0}$ to $\sin(\theta/2)$ for the original (native) DNA and products of its enzymatic degradation.^[139] The constancy of slope of the straight lines in Fig. 21 indicates that the density M/L does not vary during the degradation of the DNA. The value cited^[139] for the molecular weight per straight-line segment of the zigzag was of the order of $(5\text{--}6) \times 10^5$.

The problem of interpreting the light-scattering data from DNA solutions, as we see it, is in a state of debate. Nevertheless, there is no doubt that the light-scattering method is promising, as applied to

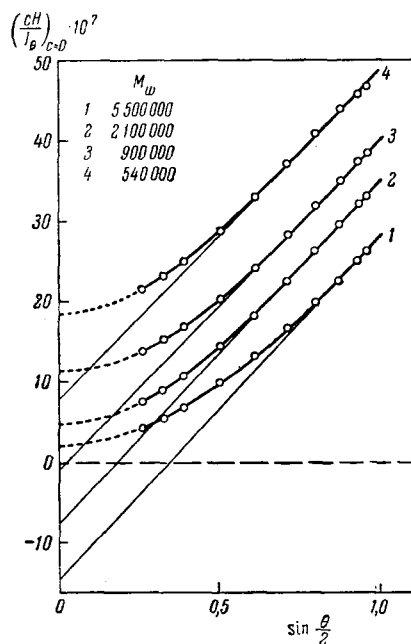


FIG. 21. The asymptotic relation of the quantity $(Hc/I_{\theta})_{c=0}$ to $\sin(\theta/2)$ for a sample of native DNA and its fragments, from the data of^[139].

Table II. Molecular weights and dimensions of PBG particles in chloroform-formamide mixture^[143]

$M \cdot 10^{-3}$	$(\overline{R^2})^{1/2}, \text{ \AA}$	$L, \text{ \AA}$	$(\overline{R^2})^{1/2}/M$	$M \cdot 10^{-3}$	$(\overline{R^2})^{1/2}, \text{ \AA}$	$L, \text{ \AA}$	$(\overline{R^2})^{1/2}/M$
130	263	910	2.02	262	528	1825	2.01
208	408	1410	1.96	358	587	2030	1.64

the problem of the DNA structure. However, this problem is quite complex, and requires for its solution the application of the entire roster of physical and physicochemical methods.

As an example of a study of a polymer having an even more rigid chain, we can cite the light-scattering measurements on solutions of poly- γ -benzyl-L-glutamate (PBG) in a chloroform-formamide mixture.^[143] Table II gives the values of M and $(\overline{R^2})^{1/2}$ determined from the intercept and initial slope of the double-extrapolation graphs (Zimm plots) for four PBG samples of the highest molecular weights. The ratio $(\overline{R^2})^{1/2}/M$ remains constant for the first three samples, but declines somewhat for the last one. The constancy of this quantity in a polymer-homolog series indicates a linear (helical) structure of the molecules of this synthetic polypeptide, since only in such a case could their dimensions be proportional to the molecular weights.

A number of theoretical and experimental studies^[24,144-146] have been concerned with the scattering from rigid anisotropic macromolecules. The fundamental relations for scattering in solutions of anisotropic rodlike particles have been derived in a theoretical paper by Horn, Benoit, and Oster.^[24] These relations have been subsequently applied in studying suspensions of tobacco mosaic virus (TMV)^[144,145] and other particles. In^[144], they measured the scattering components $(\mathcal{H}_V)_{\theta=0}$ and $(\mathcal{V}_V)_{\theta=0}$ for TMV suspensions by extrapolation to zero angle, and found the depolarization of the scattering at zero angle $\Delta_V(0^\circ) = (\mathcal{H}_V/\mathcal{V}_V)_{\theta=0}$. From $\Delta_V(0^\circ)$, they calculated by (53) and (54) the optical anisotropy δ^2 which turned out to be 0.184. Then, by comparing the theoretical variation of the function $P_V^{\mathcal{V}_0}(\theta)$ [Eq. (35)] corresponding to $\delta^2 = 0.184$ and to various relative lengths L/λ of the rods with the experimental points (Fig. 22), they showed that $L/\lambda = 0.7$. This gives for TMV: $L = (2300 \pm 200) \text{ \AA}$. According to^[146], one must likewise have a prior knowledge of the anisotropy δ^2 in determining the dimensions of rodlike anisotropic particles directly from the initial slope of the double-extrapolation graph, since here the initial slope is determined not by the mean radius of gyration but by the quantity

$$\overline{R^2} \left(1 - \frac{2\sqrt{2}\delta}{5} + \frac{10\delta^2}{35} \right).$$

Nevertheless, the determination of the length of TMV particles from the double-extrapolation graphs

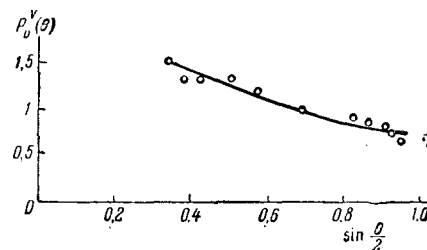


FIG. 22. A comparison of the theoretical curve $P_V^{\mathcal{V}_0}(\theta)$ and the experimental points $(\mathcal{V}_{\theta V}^{\mathcal{V}_0}/\mathcal{V}_{\theta V_0})_{\theta=0}$ ($\delta^2 = 0.184$ and $L/\lambda = 0.7$) for solutions of tobacco mosaic virus.^[144]

gives $L = 3200 \text{ \AA}$,^[195] i.e., a value greater than that obtained in^[144] upon taking the anisotropy into account. The value $L = 3200 \text{ \AA}$ agrees better with the data obtained by the hydrodynamic methods (sedimentation, viscosity) and electron microscopy. We also note that, if the greater value of the depolarization factor Δ_h of the massive TMV particles ($M \approx 40 \times 10^6$) obtained in^[144] can be ascribed to their quadrupole emission, then the value $\Delta_V(0^\circ) = 0.55$ ^[144] corresponds to an intrinsic anisotropy of TMV particles not agreeing with other data. In fact, the anisotropy $\delta^2 = 0.184$ corresponds to a difference in the principal polarizabilities of the particle $(\alpha_1 - \alpha_2) \approx 3.5 \times 10^{-18}$. A direct method of determining the anisotropy (flow birefringence) gives a value of $(\alpha_1 - \alpha_2)$ an order of magnitude smaller^[147] (see also^[8], Chap. VIII, Sec. 2). The reasons for this discrepancy are not yet clear.

In^[148], measurement of the depolarized scattering component \mathcal{H}_V is used to study the gradual decrease in rigidity of short chain molecules with increasing molecular weight. Let δ_0^2 be the anisotropy per link of a chain molecule consisting of N links. Then, according to^[148],

$$\left. \begin{aligned} \mathcal{V}_0 &= \mathcal{V}_{v0} \left[1 + \frac{2}{5} \frac{\delta_0^2}{N^2} \sum_{i,j} \frac{3a_{ij}^2 - 1}{2} \right], \\ \mathcal{H}_0 &= \mathcal{H}_{h0} = \mathcal{V}_{v0} \frac{3}{10} \frac{\delta_0^2}{N^2} \sum_{i,j} \frac{3a_{ij}^2 - 1}{2}, \end{aligned} \right\} \quad (84)$$

where \mathcal{V}_{v0} is the light intensity scattered by a chain of N isotropic links of the same mean polarizability, and a_{ij}^2 is the mean square of the cosine of the angle between the principal polarizability axes of the links i and j of the chain. The summation is performed over all possible pairs of links. For rodlike particles, $|a_{ij}| = 1$, and the double summation gives N^2 . For sufficiently long chains, approximating Gaussian coils,

the double summation gives $N(1+\varphi)$, where the constant φ is determined by the nature of the short-range interaction in the chain. According to the general relation (5), $\mathcal{V}_V/c \sim N$. If we plot the quantity \mathcal{H}_V/c as a function of N (or of M , which is the same thing), then in the region of transition from rods to Gaussian coils, \mathcal{H}_V/c must decline and approach a constant value. Figure 23 (from [148]) shows that such a variation in the depolarized scattering component is actually observed in solutions of low-molecular-weight fractions of polystyrene. The quantity \mathcal{H}_V/c attains a constant value at a molecular weight ≈ 5000 , corresponding to the relatively low degree of polymerization $N \approx 50$. Thus, measurements of the depolarization of scattering can be used to study the rigidity of relatively short chains.

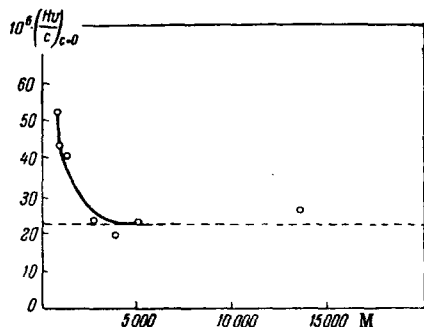


FIG. 23. The approach to the asymptote of the quantity $(H_V/c)_{c=0}$ with increasing molecular weight for the depolarized scattering component of solutions of low-molecular-weight polystyrene. [148]

10. THE STUDY OF STEREOSPECIFIC MACROMOLECULES

As is known, the study of stereoregular polymers is complicated by their considerably poorer solubility as compared with their atactic homologs. Besides, the solutions of isotactic polymers are often contaminated with impurities of colloidal nature: residues of the organometallic catalysts, as well as insoluble microcrystallites. This requires especially careful purification of the solutions. Owing to these additional difficulties, the amount of experimental material obtained on isotactic polymers is still very limited. A few authors have measured the light scattering of the isotactic stereoisomers of polystyrene, [149-151] polymethylmethacrylate, [152] polypropylene, [153-155] and poly-*n*-butene. [156] All of these measurements were performed in good solvents. The most essential of the obtained results are the following. We can consider it to be firmly established that in good solvents the relation between $[\eta]$ and M does not differ for the iso- and atactic isomers. [150-152, 154, 156] This is evidence that the hydrodynamic properties of the macromolecules of the stereoisomers determining the value of the viscosity $[\eta]$ are the same.

We can also consider it to be established that the relation of the second virial coefficient A_2 to M in good solvents differs in nature for iso- and atactic isomers. The straight line $\log A_2 \sim \log M$ shows a smaller slope for an isotactic polymer than for the atactic one. [150, 151, 154] This is illustrated by Fig. 24, which was obtained for polypropylene in [154]. The same result has been obtained for polystyrene and poly-*n*-butene by the osmotic method. [156, 157]

Reliable determinations of coil dimensions $(\bar{h}^2)^{1/2}$ for stereoregular polymers are extremely scarce. The coil dimensions of isotactic polystyrene and polypropylene measured in [150, 154] do not differ in good solvents from those of the atactic isomers of the same M .

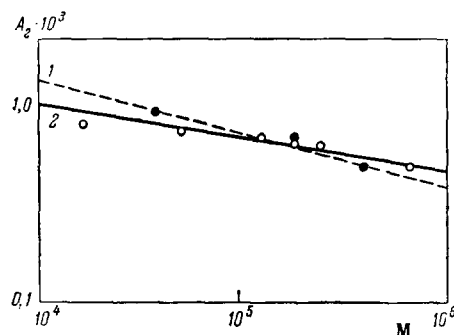


FIG. 24. The relation of the second virial coefficient A_2 of solutions of isotactic (2) and atactic (1) polypropylene in 1-chloronaphthalene to the molecular weight M (from the data of [154]).

The modern thermodynamic theories of polymer solutions establish a relation between the quantities $(\bar{h}^2)^{1/2}$, M , A_2 , and α (or $[\eta]$, M , A_2 , and α). Thus, they permit one to calculate the unperturbed coil dimensions $(\bar{h}_0^2)^{1/2}$ from measurements in good solvents. [58] It is pointed out in [150, 156] that the smaller values of A_2 (for equal $[\eta]$ and M) of the isotactic polymers imply smaller values of α , and hence, a value of $(\bar{h}_0^2)^{1/2}$ that is 15-20% larger than for the atactic polymers. An experimental confirmation of this conclusion would imply the establishment of a relation between the flexibility of polymer chains and their stereoisomerism. This would be of importance in determining more exactly the nature of the short-range interaction in the chains. A direct test of this conclusion by direct measurement of $(\bar{h}_0^2)^{1/2}$ in an ideal solvent is practically ruled out. However, we might hope that for certain isotactic polymers it would prove possible to measure the intrinsic viscosity $[\eta]_0$ in an ideal solvent; this would make considerably fewer demands on the purification of the solutions. In view of the direct relation between $[\eta]_0$ and $(\bar{h}_0^2)^{1/2}$, the important problem of the effect of stereoisomerism on the flexibility of chains probably could be solved in this way.

11. THE STUDY OF COPOLYMERS

Interest has arisen in the theoretical treatment of the problem of light scattering of copolymers in con-

nection with the experimental fact that their solutions show anomalously intense scattering and a very small refractive increment.^[158] In order to explain it, the idea has been advanced that this anomaly involves inhomogeneity of composition in the copolymer^[159] (we shall refer to inhomogeneity of a copolymer with regard to the chemical composition of its macromolecules as compositional inhomogeneity or compositional dispersion).

Based on an initial assumption that the refractive increment of a copolymer solution is a linear function of its composition, Stockmayer et al.,^[160] and later Bushuk and Benoit^[161,162] have developed a theory of light scattering by solutions of copolymers. In^[161,162], this theory was first applied for a quantitative study of compositional dispersion of copolymers.

We introduce the following notation. Let the copolymer contain weight concentrations c_A and c_B of components A and B. Let the refractive increments of the copolymer and the homopolymers in the given solvent be denoted by ν , ν_A , and ν_B , respectively. Then, for dilute solutions^[160]

$$\nu = x\nu_A + (1-x)\nu_B, \quad (85)$$

where $x = c_A / (c_A + c_B)$ is the weight fraction of component A.

We shall denote by M_{app} the apparent molecular weight of the copolymer obtained by the ordinary extrapolation to zero concentration according to the general relation (10), by M_w the true (weight-average) molecular weight of the copolymer, and by M_A and M_B the weight-average molecular weights of components A and B in the copolymer. In a simple fashion we can derive the following equations:

$$M_{app} = \left(\frac{\nu_A \nu_B}{\nu^2} \right) M_w + \left[\frac{\nu_A (\nu_A - \nu_B)}{\nu^2} \right] x M_A + \left[\frac{\nu_B (\nu_B - \nu_A)}{\nu^2} \right] (1-x) M_B, \quad (86)$$

or

$$M_{app} = M_w + 2 \frac{\nu_A - \nu_B}{\nu} P + \left(\frac{\nu_A - \nu_B}{\nu} \right)^2 Q, \quad (87)$$

where P and Q are parameters of the compositional inhomogeneity of the copolymer, equal to

$$P = \sum_{i,j} \gamma_i M_{ij} \delta x_i = \frac{1}{2} [(1-x)(M_w - M_B) - x(M_w - M_A)] \quad (88)$$

and

$$Q = \sum_{i,j} \gamma_i M_{ij} \delta x_i^2 = x(1-x)(M_A + M_B - M_w); \quad (89)$$

Here $\delta x_i = x_i - x$ is the deviation in composition of the i -th particle from the mean composition x , and γ_i is the relative concentration (fraction) of the particles having the composition x_i . In the expressions for P (88) and Q (89), the summation is performed twice: over the differing compositions of the molecules (i), and over the differing molecular weights (j).

On the basis of Eq. (87), we can in principle calculate the three unknown quantities M_w , P, and Q (or M_w , M_A , and M_B) from measurements of M_{app} in three solvents. If we then plot this quantity (or M_{app}/M_w) as a function of the argument $(\nu_A - \nu_B)/\nu$ (i.e., as a function of n_0), then the points must lie on a parabola.

The parameters P and Q lie within the limits

$$-xM_w \leq P \leq (1-x)M_w, \quad 0 \leq Q \leq M_w[x(1-x)].$$

The parameter P characterizes the tendency to variation in the composition of the chains with increasing molecular weight of the copolymer. It can be either positive or negative, depending on which of the components (A or B) predominates in the high-molecular-weight fraction of the copolymer.

The parameter Q (or more conveniently, Q/M_w) characterizes the mean compositional dispersion of the copolymer. This parameter is always positive, and the maximum possible value of Q/M_w is $x(1-x)$.

As a measure of the compositional dispersion of copolymers, Bushuk and Benoit have introduced the quantity Q/Q_{max} .

We shall discuss some special cases.

Copolymer having chains of homogeneous composition. In this case, $\delta x_i \equiv 0$, and hence $P = Q \equiv 0$, and (87) implies $M_{app} = M_w$. Equations (88) and (89) give for this special case $M_A = xM_w$ and $M_B = (1-x)M_w$.

A mixture of two homopolymers A and B having molecular weights M_A and M_B and relative concentrations γ_A and γ_B . In this case,

$$\left. \begin{aligned} P &= x(1-x)(M_A - M_B), \\ Q &= x(1-x)[(1-x)M_A + xM_B]. \end{aligned} \right\} \quad (90)$$

Equation (87) gives

$$M_{app} = \frac{1}{\nu^2} (\nu_A^2 \gamma_A M_A + \nu_B^2 \gamma_B M_B). \quad (91)$$

If we choose n_0 , γ_A , and γ_B such that $\nu \approx 0$, then here $M_{app} \approx \infty$. If we choose a solvent in which $\nu_A = 0$ (or $\nu_B = 0$), then from (91) we can calculate the weight-average molecular weight of the second homopolymer M_B (or M_A). As we see from (90), when $M_A = M_B$, the parameter P becomes zero (we note that if a copolymer is monodisperse in mass, again $P = 0$). The parameter Q/M_w attains its maximum value $x(1-x)$ for a mixture of homopolymers (having $M_A = M_B = M_w$). Such a mixture is the limiting case of compositional inhomogeneity of a copolymer.

This theory has been tested by Bushuk and Benoit^[161,162] on three objects: mixtures of polystyrene with polymethylmethacrylate, random, and block S-MMA copolymers. The results agreed with the theory. The compositional dispersion turned out to be near the maximum ($Q/Q_{max} = 0.72$) for the random copolymer, and very small for the block polymer ($Q/Q_{max} = 0.05$), in accord with the conditions of synthesis of the latter.

In [163], the compositional dispersion was studied in a random S-MMA copolymer and a series of fractions of it obtained in two solvent-precipitant systems. One of these (I) was sensitive to the composition of the macromolecules, and the other (II) was not very sensitive to composition. [164] In agreement with the theory of fractionation of copolymers in such systems, [165] the study of the compositional dispersion of the fractions made in [163] showed that the first fractions from system I have a smaller dispersion ($Q/Q_{\max} \approx 0.30$), while the last fractions have a somewhat greater dispersion than the original sample ($Q/Q_{\max} \approx 0.60$). The fractions from system II did not show such a difference in dispersion. Figure 25 shows the relation of M_{app}/M_w to $(\nu_A - \nu_B)/\nu$ obtained in [163] by studying the original copolymer in five solvents having n_0 from 1.380 to 1.601.

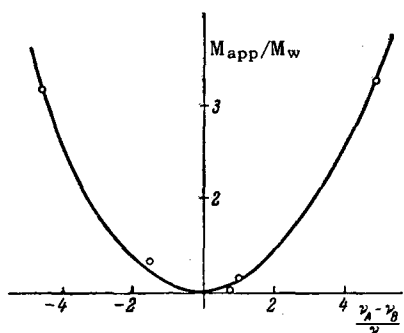


FIG. 25. The experimental relation of M_{app}/M_w to $(\nu_A - \nu_B)/\nu$ for an unfractionated random S-MMA copolymer (21:79). [163]

The theory of light scattering by copolymer solutions holds both for small and large macromolecules, under the condition (for the latter) that one extrapolates the results to zero scattering angle. It is valid for copolymers of any structure: random copolymers, block polymers, and graft polymers.

The problem of the angular dependence of the light scattering of copolymer solutions has been discussed by Benoit and Wippler. [166] In [166, 167], relations are derived that are necessary in determining the coil dimensions of copolymers by light scattering.

Let R_{app}^2 denote the mean square radius of gyration of the copolymer molecules, as determined from the initial slope of the $(Hc/I_{\theta_V})_{c=0}$ curve. Then, the following equation holds for this quantity:

$$R_{\text{app}}^2 = \frac{1}{\nu^2} [x^2 \nu_A^2 R_A^2 + (1-x)^2 \nu_B^2 R_B^2 + 2x(1-x) \nu_A \nu_B R_{AB}^2], \quad (92)$$

where x , ν , ν_A , and ν_B have their previous meanings, R_A^2 is the mean square radius of gyration of component A in the copolymer molecules, and R_B^2 is the same quantity for component B,

$$R_{AB}^2 = \frac{1}{2} (R_A^2 + R_B^2 + l^2), \quad (93)$$

and l^2 is the mean square distance between the centers of gravity of components A and B in the copolymer molecules.

If we introduce the variable $y = x\nu_A/\nu$, then we can write (92) in the form

$$R_{\text{app}}^2 = yR_A^2 + (1-y)R_B^2 + y(1-y)l^2, \quad (94)$$

This implies that, in general, R_{app}^2 is a quadratic function of y (i.e., of the refractive index of the solvent). For copolymers of concrete structure, R_{app}^2 will be expressed in various ways in terms of R_A^2 and R_B^2 as a function of the quantity l^2 . It is not hard to envision the limiting cases in which l^2 will have its greatest and least values. For a random copolymer, the centers of gravity of components A and B in the molecules will coincide on the average, and $l^2 = 0$. The other limiting case is a block polymer whose molecules consist of only two blocks, A and B. It was shown in application to [167] that in this case $l^2 = 2(R_A^2 + R_B^2)$. Hence,

$$0 \leq l^2 \leq 2(R_A^2 + R_B^2).$$

In analyzing the structure of a copolymer, a convenient step is to form the product $M_{\text{app}}R_{\text{app}}^2$, which equals

$$M_{\text{app}}R_{\text{app}}^2 = \frac{M_A R_A^2}{x} y^2 + \frac{M_B R_B^2}{1-x} (1-y)^2 + 2y(1-y) \frac{M_{AB} R_{AB}^2}{x(1-x)}, \quad (95)$$

where

$$M_{AB} = 0.5[M_w - xM_A - (1-x)M_B]. \quad (96)$$

Let R^2 be the mean square geometric radius of gyration of the copolymer (assuming that all the segments have the same mass). Then

$$M_{\text{app}}R_{\text{app}}^2 = \frac{\nu_A \nu_B}{\nu^2} M_w R^2 + \frac{\nu_A (\nu_A - \nu_B)}{\nu^2} x M_A R_A^2 + \frac{\nu_B (\nu_B - \nu_A)}{\nu^2} (1-x) M_B R_B^2. \quad (97)$$

Equations (92) and (97) show that in principle we can determine R^2 , R_A^2 , and R_B^2 (or R_A^2 , R_B^2 , and R_{AB}^2) from measurements in three solvents. According to (95), $M_{\text{app}}R_{\text{app}}^2$ is a quadratic function of y , or a parabola with a vertical axis. The ordinates corresponding to abscissas of unity and zero give the quantities $M_A R_A^2/x$ and $M_B R_B^2/(1-x)$, which permit us to calculate R_A^2 and R_B^2 . The direction of convexity of the parabola is determined by the coefficient D of the y^2 term in (95):

$$D = \frac{M_A R_A^2}{x} + \frac{M_B R_B^2}{1-x} - \frac{2M_{AB} R_{AB}^2}{x(1-x)}. \quad (98)$$

Let us introduce, along with $\delta x_i = x_i - x$, the molecular quantity $l_i^2 = 2R_{ABi}^2 - R_{Ai}^2 - R_{Bi}^2$. Then we can write (98) in the form:

$$D = \frac{\sum \gamma_i M_i \delta x_i}{x^2 (1-x)^2} [x_i (1-x) R_{Ai}^2 - (1-x_i) x R_{Bi}^2] - \frac{\sum \gamma_i M_i x_i (1-x_i) l_i^2}{x(1-x)}. \quad (98a)$$

Equations (98) and (98a) permit us to analyze the vari-

ation in the quantity $M_{\text{app}}R_{\text{app}}^2$ as a function of y (n_0 of the solvent) for concrete copolymer structures. We shall discuss some important cases.

a) Random copolymer. In this case, as was stated above, we can assume $l^2 \equiv 0$. In addition, $R_{\text{Ai}}^2 = R_{\text{Bi}}^2$. Under these conditions, D is simplified to the quantity

$$D = \frac{\sum \gamma_i M_i \delta x_i^2}{x^2 (1-x)^2} R_{\text{Ai}}^2,$$

which is essentially positive. For a copolymer having compositional dispersion, this gives a relation of $M_{\text{app}}R_{\text{app}}^2$ to y in the form of a parabola convex downward. For a random copolymer with homogeneous chain composition ($\delta x_i \equiv 0$), $D = 0$, and the parabola degenerates into a straight line.

b) Block polymer of the type AB. In this case, $l^2 = 2(R_{\text{A}}^2 + R_{\text{B}}^2)$, and by applying (93), (96), and (98), we can convince ourselves that D is negative. The $M_{\text{app}}R_{\text{app}}^2$ curve is a parabola convex upward.*

c) Graft polymer. The relation between the quantities R_{app}^2 , R_{A}^2 , and R_{B}^2 has been derived only for a graft polymer of the simplest structure: one branch of component B grafted to a chain of component A. The following equation was derived in [166] for this case (considering that the branch B can be grafted onto any point of the chain A):

$$R_{\text{app}}^2 = y^2 R_{\text{A}}^2 + (1-y)^2 R_{\text{B}}^2 + 3y(1-y) \left(R_{\text{B}}^2 + \frac{2}{3} R_{\text{A}}^2 \right). \quad (99)$$

By using the general relation (94), we can easily show, upon converting (99) to the form

$$R_{\text{app}}^2 = y R_{\text{A}}^2 + (1-y) R_{\text{B}}^2 + y(1-y) (R_{\text{A}}^2 + 2R_{\text{B}}^2), \quad (99a)$$

that for such a graft polymer, $l^2 = R_{\text{A}}^2 + 2R_{\text{B}}^2$. Upon applying (93), (96), and (98), we can convince ourselves that the coefficient D of y^2 in (95) is negative, and the curve of $M_{\text{app}}R_{\text{app}}^2$ as a function of y is a parabola convex upward. This is to be expected, since the case of a graft polymer having one grafted branch structurally resembles a block polymer of the type AB.

d) Mixture of homopolymers. In this case, $M_{\text{W}} = xM_{\text{A}} + (1-x)M_{\text{B}}$, and $M_{\text{AB}} = 0$. Hence,

$$D = \frac{M_{\text{A}}R_{\text{A}}^2}{x} + \frac{M_{\text{B}}R_{\text{B}}^2}{1-x} > 0$$

and the $M_{\text{app}}R_{\text{app}}^2$ curve is a parabola convex downward. This case coincides with that of a random copolymer having the extreme of compositional inhomogeneity of its chains.

*A recent paper^[194] developing the results obtained in [166] has shown that for a two-block polymer of the type AB, the curves of the relation of the quantity HcM_v^2/I to the argument $(16\pi^2 \times (R^2/\lambda^2) \sin^2(\theta/2))$ have a positive initial slope if the value of y is within the range from 0.5 to 1.2. At larger values of y , these curves have a negative initial slope, and pass through a minimum. As an example of an experimental confirmation of this calculated result, the authors of [194] present a graph of $I_{\theta} \sim \sin^2(\theta/2)$ for the scattering from a PS-PMMA block polymer (of the type BAB) in styrene, showing a maximum at $\sin^2(\theta/2) \approx 0.07$.

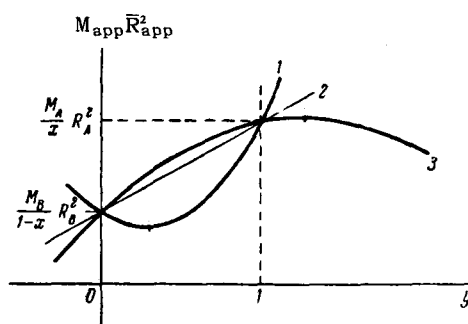


FIG. 26. Theoretical curves of the relation of the product $M_{\text{app}}R_{\text{app}}^2$ to the quantity $y = x\nu_{\text{A}}/\nu$ for: a random copolymer having compositional inhomogeneity (1), a random copolymer of homogeneous composition (2), and a block copolymer (3). [168]

Figure 26 shows the variation of the value of the product $M_{\text{app}}R_{\text{app}}^2$ as a function of y for the cited cases.

An analysis of the structure of block and graft polymers of more complex structure from light-scattering data has not yet been developed. We can only state that in [167] the values of R_{AB}^2 and l^2 were calculated for block polymers consisting of n blocks of A alternating with an equal number of blocks of B. If the A blocks contain N segments of length a , and the B blocks contain K segments of length b , then

$$l^2 = \frac{1}{3n} (Na^2 + Kb^2).$$

Understandably, as the number n of blocks increases, $l \rightarrow 0$, and we go over to a case similar to that of a random copolymer having uniform chain composition, for which the $M_{\text{app}}R_{\text{app}}^2$ parabola degenerates into a straight line. We can state only some general notions with regard to graft polymers. Graft polymers containing several B branches grafted onto a main A chain will give an $M_{\text{app}}R_{\text{app}}^2$ curve similar to that of a block polymer having a small number of blocks. Graft polymers containing a very large number of short B branches grafted onto an A chain will give an $M_{\text{app}}R_{\text{app}}^2$ curve similar to that for a random copolymer. The intermediate case for a graft polymer will be more complex.

In the most general case, in which the copolymer is polydisperse in mass, composition, and structure, it is hard to predict the variation of the $M_{\text{app}}R_{\text{app}}^2$ curve in advance.

References [167, 168] give experimental data on the relation of $M_{\text{app}}R_{\text{app}}^2$ to y for a random copolymer, a block polymer, and a mixture of homopolymers; these data agree with the theoretical ideas presented here. From the experimental data, they directly calculated in the corresponding cases the quantities R_{A}^2 , R_{B}^2 , R_{AB}^2 , and l^2 , which are directly involved in the molecular structure of the copolymer. They showed thereby that one can use the light-scattering method for detailed study of copolymer molecules. However, we must point out that the practical realization of this

possibility depends on the optical properties of the components of the copolymer. A successful analysis of the structure of a copolymer is possible only when the refractive indices of the components differ sufficiently. If the values of ν_A and ν_B are close to one another, an analysis of the structure of the copolymer is impossible. Nevertheless, as Eqs. (86) and (97) show, when $\nu_A = \nu_B$, we can obtain the true values of the molecular weight M_w and the radius of gyration R^2 of the copolymer, regardless of the refractive index of the solvent (with the exception, of course, of $\nu = 0$, and of too small values of ν).

We note that the method developed in [167] of determining the dimensions of copolymer molecules by light scattering requires some qualifications. The point is that the determination using (92) or (97) of the values of R_B^2 , R_A^2 , and R_{AB}^2 (or R^2) from light-scattering measurements in three solvents assumes that these quantities have the very same values in all three solvents. In addition, if the set of solvents includes both poor and good solvents (for one or both components of the copolymer), then certain of the quantities R^2 , R_A^2 , and R_B^2 (or all three) can vary considerably in going from one solvent to another. Understandably, the neglect of this fact cannot help but affect the accuracy of determination of the dimensions by Eq. (92) or (97). From the standpoint of successfully applying the method developed in [167], it is preferable to include in the set of solvents (having differing n_0) only those that are good solvents for both components of the copolymer (if such a choice is possible).

There are practically no data in the literature on light-scattering studies of graft polymers. In [169], which was concerned with studying a methyl methacrylate-styrene graft polymer, the molecular weight M_B of the grafted polystyrene was determined by the light-scattering method. For this purpose, benzene, in which $\nu_A = 0$, was chosen as the solvent. In line with (86), M_B was calculated here by the relation

$$M_B = \frac{\nu^2}{\nu_B^2} \frac{1}{1-x} M_{app},$$

while the value of x was determined by refractometry.

12. THE STUDY OF INTERMOLECULAR INTERACTIONS (SECOND VIRIAL COEFFICIENT)

The second virial coefficient A_2 entering into the general scattering equation (3a) characterizes the degree of deviation of the solution from ideal behavior (van't Hoff's law), and is a qualitative measure of the intermolecular interaction in solution. Modern thermodynamic (and statistical) theories of polymers [32, 170] relate A_2 to the molecular parameters. Hence, the study of A_2 is important in a well-rounded study of the properties and structure of macromolecules in solution.

The existing theories of A_2 as a measure of the in-

termolecular interactions introduce the so-called "effective excluded volume" v_0 of a segment. This quantity involves the impossibility of a given segment of a polymer molecule occurring in a volume element of the solution occupied by another segment (of the same or an adjacent molecule). It is defined as

$$v_0 = 4\pi \int_0^\infty (1 - e^{-\frac{\varphi(r)}{kT}}) r^2 dr, \quad (100)$$

where $\varphi(r)$ is the interaction potential of two segments occurring at a distance r apart. As Stockmayer [171] has pointed out, the exact form of the potential $\varphi(r)$ plays no essential role, since the excluded volume v_0 depends very weakly on the form of the function $\varphi(r)$.

In terms of the quantity v_0 , A_2 can be represented in the form [170]:

$$A_2 = \frac{N_A}{2} \frac{v_0}{M_0^2} F(z), \quad (101)$$

where M_0 is the molecular weight per segment (link), and $F(z)$ is a function of the quantity z proportional to the number of contacts between segments per unit volume, which equals

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \frac{N^{1/2} v_0}{b^3}; \quad (102)$$

here N is the number of segments (links) in the polymer molecule, and b is the effective length of the connection between consecutive segments (links) of the chain.

At the Θ -point, $\varphi(r) = 0$, and hence, $v_0 \equiv 0$ and $z \equiv 0$, whereby $F(0) \equiv 1$.

The form of the function $F(z)$ depends on the molecular model adopted in the given theory, which determines the probability of contacts (interactions, collisions) between segments (links), and also depends on how fully we account for the number of such contacts. If we limit ourselves to single contacts only (contacts of one segment of the given macromolecule with one of the segments of an adjacent macromolecule, or a "pair interaction"), then, regardless of the molecular model applied,

$$F(z) = 1 \text{ and } A_2 = \frac{N_A}{2} \frac{v_0}{M_0^2}.$$

In the modern theories of A_2 , methods have been developed of taking into account double and triple contacts (simultaneous contact of two or three pairs of segments of the interacting macromolecules). A strict account of interactions of high order (triple and higher) involves considerable mathematical difficulties.

In the most widely-known theory of Flory, [32] which he has developed in conjunction with Krigbaum [102] and Orofino, [58] each of the interacting macromolecules is represented by the model of a cloud of segments. Its density is spherically symmetrical with respect to the center of inertia, and decreases according to a Gaussian law. This model gives the following ex-

pression for $F(z)$:

$$F(z) = \frac{\ln \left(1 + \frac{3\sqrt{3\pi}}{4} z\alpha^{-3} \right)}{\frac{3\sqrt{3\pi}}{4} z\alpha^{-3}}, \quad (103)$$

where

$$\alpha^5 - \alpha^3 = \frac{3\sqrt{3}}{2} z, \quad (104)$$

and at small z ,

$$F(z) = 1 - 1.15z + 6.25z^2 - \dots, \quad (103a)$$

where α is the swelling coefficient of the coil in going from an ideal solvent ($A_2 = 0$) to the given solvent.

As Stockmayer has shown,^[172] the coefficient $3\sqrt{3}/2$ in (104) must be replaced by $134/105$ to reconcile the theory with the experimental data. With this value of the coefficient, $F(z)$ can be represented at small z in the form of the series

$$F(z) = 1 - 1.15z + 3.97z^2 - \dots \quad (103b)$$

We note that in representing the function $F(z)$ as a power series, the corresponding terms of the series take into account the contribution to A_2 made by double (the z term), and then triple (the z^2 term), etc., intermolecular contacts (interactions).

Following Flory and his associates,^[102,58] a number of other authors have derived expressions for the function $F(z)$ by using a more realistic model or by making a strict statistical account of double and triple intermolecular interactions.^[173-180] The power series obtained in the cited studies for $F(z)$ converge poorly, so that they can be used only for small z ($z < 0.15$), i.e., in the vicinity of the Θ -point.

In order to compare the theory of A_2 with experiment, one studies experimentally the relation of A_2 to the temperature and molecular weight of the polymer. In such a comparison, one must express the excluded volume v_0 per segment in the expression (101) for A_2 in terms of the thermodynamic parameters of the polymer-solvent system. Here we can obtain^[32]

$$v_0 = \frac{2v_s^2}{V_1} \psi_1 \left(1 - \frac{\Theta}{T} \right), \quad (105)$$

where v_s is the volume of a segment, V_1 is the volume of a solvent molecule, ψ_1 is a parameter characterizing the entropy of mixing of the polymer with the solvent,^[32] and Θ is the temperature at which $A_2 = 0$ (the Θ -temperature).

If we substitute (105) into (102), the argument z of the function $F(z)$ takes on the form

$$z = \left(\frac{3}{\pi} \right)^{3/2} \frac{\bar{v}^2}{V_1} \left(\frac{\bar{h}_0^2}{M} \right)^{-3/2} \psi_1 \left(1 - \frac{\Theta}{T} \right) M^{1/2}, \quad (106)$$

if we bear in mind that $v_s = \bar{v}M_0/N_A$, and $Nb^2 = \bar{h}_0^2$ (\bar{v} is the partial specific volume of the polymer in the solution, and v_1 is the molar volume of the solvent). Substituting (105) into (101), we have

$$A_2 = \frac{\bar{v}^2}{v_1} \psi_1 \left(1 - \frac{\Theta}{T} \right) F(z). \quad (107)$$

Since \bar{v} , V_1 , ψ , and Θ are constants for a given polymer-solvent system, Eq. (107) makes evident the relation of A_2 to the temperature T and the molecular weight, in terms of z . In the single-contact approximation ($F(z) = 1$), A_2 is independent of the molecular weight (and correspondingly independent of the molecular model used). In the double-contact approximation (the linear term of $F(z)$), A_2 is proportional to $(1 - KM^{1/2})$, and in the further approximations, the relation of A_2 to M is more complex.

Many authors have carried out tests of the theory of A_2 , but for the most part with a limited experimental material. The studies of Kirste and Schulz,^[181] and especially^[182], have been concerned with systematically studying the relation of A_2 in PMMA solutions to the molecular weight and the temperature. They measured A_2 for four PMMA fractions (having $M = 3 \times 10^4$; 2.1×10^5 ; 1.1×10^6 ; and 4.6×10^6) in various solvents and at different T .

The results of the comparison of A_2 with theory proved to favor the theory of Isihara and Koyama.^[173] The temperature-dependence of A_2 in the region where it is positive is also well described by the Flory-Krigbaum-Orofino theory. However, in the region $A_2 < 0$, the latter strongly disagrees with experiment (Fig. 27) (as do all the other theories except that of Isihara and Koyama).

Kirste and Schulz have come to the conclusion that a strict account of the interactions is not necessary for an adequate theory of the second virial coefficient (its necessity is implied by the existence of the bonds

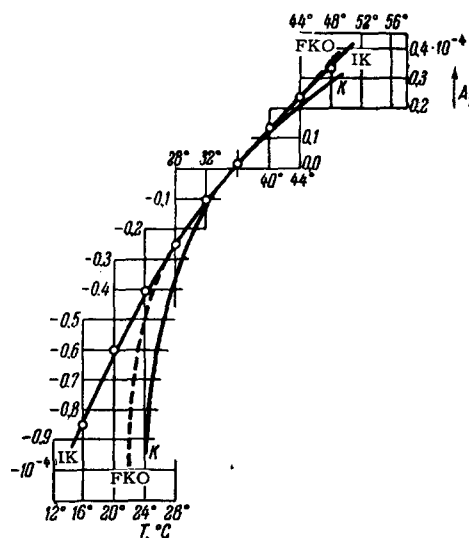


FIG. 27. The temperature-dependence of the second virial coefficient A_2 of solutions of a polymethylmethacrylate fraction ($M = 2.1 \times 10^5$) in butyl chloride; comparison with the theories of Flory, Krigbaum, and Orofino (FKO), Isihara and Koyama (IK), and Casassa (C).^[182]

between the links in the actual polymer chain), and that a model of the coil in the form of a cloud of segments with a Gaussian density distribution is quite sufficient for a satisfactory theory of A_2 .^[182] This conclusion seems premature to us, in spite of the important significance of the experimental material obtained in ^[182]. Further systematic studies of the relations $A_2(M)$ and $A_2(T)$ in other polymer-solvent systems are necessary. In this regard, we should refer to the study of Schulz and his associates,^[183,184] in which the idea is developed of separating A_2 into entropic and enthalpic portions for exothermic solutions (polystyrene-benzene), whereas the Isihara-Koyama theory is valid in endothermic solutions (PMMA-butyl chloride).

A most important result of the modern thermodynamic theory of polymer solutions is the establishment of a relation between A_2 and $(\bar{h}^2)^{1/2}$. We can easily derive from Eqs. (106) and (107) (bearing in mind the fact that $\bar{h}^2 = \alpha^2 \bar{h}_0^2$):

$$A_2 = \frac{2^{1/2} \pi^{3/2} N_A (\bar{h}^2)^{3/2}}{3^{3/2} M^2} \Psi(\alpha), \quad (108)$$

where

$$\Psi(\alpha) = \frac{z}{\alpha^3} F(z). \quad (109)$$

It is quite important to know the exact form of the function $\Psi(\alpha)$. In fact, since all the quantities entering into (108), except for $\Psi(\alpha)$, are determined experimentally, a knowledge of the function $\Psi(\alpha)$ should permit us to determine α from measurements of A_2 , M , and $(\bar{h}^2)^{1/2}$ in a good solvent. This implies also the determination of the unperturbed coil dimensions $(\bar{h}_0^2)^{1/2}$ in an ideal solvent, characterizing the flexibility of the chains. In particular, this is important in stereoregular polymers, for which one cannot obtain solutions in ideal solvents.

According to (109), each function $F(z)$ in the above-mentioned theories of the second virial coefficient corresponds in principle to its own particular function $\Psi(\alpha)$. Figure 28, taken from ^[185], shows the variation of the function $\Psi(\alpha)$ according to some of the existing theories. To test the theoretical $\Psi(\alpha)$ functions, one must use measurements of A_2 , M , $(\bar{h}^2)^{1/2}$, and α made by the light-scattering method with double extrapolation of the results of the measurements. The most desirable region of measurements for this purpose is that of large α values (good solvents and large M). Here the determinations of $(\bar{h}^2)^{1/2}$ and α must necessarily take into account the influence of the volume effects. At present, such measurements are very few in number. Figure 28 contains the experimental data collected in ^[185], which we have supplemented with those from ^[38]. The experimental data in the region $\alpha > 1.5$ are still clearly insufficient to solve the problem of the true variation of the function $\Psi(\alpha)$. In addition, the very concept of "unperturbed dimensions" $(\bar{h}_0^2)^{1/2}$ of a coil, and hence also of α , perhaps should

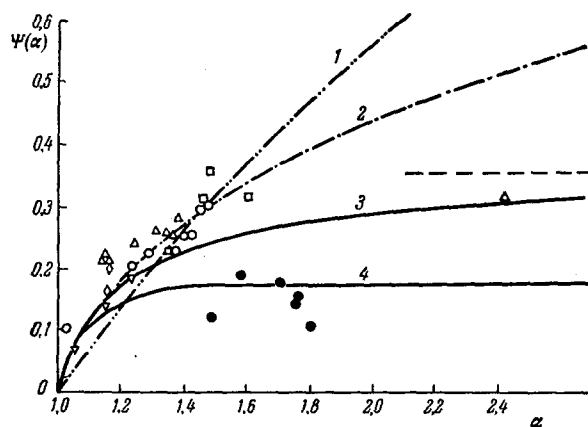


FIG. 28. The variation of the function $\Psi(\alpha)$ with increase in the swelling coefficient α of the coils according to the theories of Flory, Krigbaum, and Orofino (1 and 2), Ptitsyn (3), and Casassa and Markovitz (4). Experimental points: Δ - polystyrene in toluene;^[59,129,197,198] \diamond - polystyrene in butanone;^[197] \circ - polyisobutylene in cyclohexane;^[198] \square - polyvinylacetate in butanone;^[72] ∇ - polystyrene in cyclohexane;^[47] \bullet - poly-2, 5-dichlorostyrene in dioxane.^[38]

be made more exact.^[186] Hence, although the experimental points occurring in the region $\alpha > 1.5$ lie below the curves 1 and 2 for $\Psi(\alpha)$, nevertheless, no conclusion on the preferability of any given function $\Psi(\alpha)$ seems to us to be sufficiently substantiated.

We shall briefly take up the problem of the "angular dependence" of the second virial coefficient. In Zimm's well-known study,^[28] which is devoted to taking into account the effect of the intermolecular interactions on the light scattering of polymer solutions, the treatment has been limited to the single-contact approximation. In this approximation, the scattering equation has the form

$$\frac{Hc}{I_0} = \frac{1}{MP(\theta)} + 2A_2c + A_3R(\theta)c^2 + \dots, \quad (110)$$

where the second term of the series expansion of I_0^{-1} in terms of the concentration is independent of the scattering angle θ . Strictly speaking, this approximation is valid only in poor solvents near the Θ -point. Albrecht^[187] and Flory and Bueche^[188] have shown that in the next approximation taking double intermolecular interactions into account, the second term in (110) now depends on the scattering angle. Flory and Bueche^[188] have considered the problem within the framework of the characteristic model of Flory's studies of a "Gaussian smoothed density". Albrecht^[187] gives a stricter statistical solution, which is limited, however, to the region of small z values or small scattering angles θ . The result of ^[187] and ^[188] differs from (110) in the appearance of a new function $Q(\theta)$ involving the mean square distance between the centers of two interacting molecules^[187] (analogously to the way that the function $P(\theta)$ involves the mean square radius of gyration of a single molecule):

$$\frac{Hc}{I_0} = \frac{1}{MP(\theta)} + 2A_2Q(\theta)c + A_3R'(\theta)c^2 + \dots \quad (111)$$

At zero scattering angle ($\theta = 0$), the interference of the light scattered from two interaction molecules vanishes (just as for intramolecular interference), and $Q(0^\circ) \equiv 1$. In the single-contact approximation, as has been stated, $Q(\theta) = 1$ independently of the scattering angle. Albrecht's solution^[187] for small z (or small angles) has the form

$$Q(\theta) = 1 - 0.296xz + \dots, \quad (112)$$

where

$$x = 16\pi^2 \frac{R^2}{\lambda^2} \sin^2 \frac{\theta}{2}$$

is the well-known argument of the Debye scattering function $P_V(\theta)$.

The less strict solution of Flory and Bueche^[188] has a wider range of applicability, including large angles θ and good solvents (large z). Flory and Bueche relate the function $Q(\theta)$ to the thermodynamic parameters of Flory's theory.^[32,58] As Albrecht points out,^[187] in the approximation involving the "Gaussian smoothed density" model used in^[188], the series for $Q(\theta)$ takes on the form

$$Q(\theta) = 1 - 0.153xz + \dots \quad (113)$$

A comparison of the coefficients in (112) and (113) reveals the degree of approximation in the study of Flory and Bueche^[188], as compared with the exact statistical treatment.^[187]

Equation (112) implies that the function $Q(\theta)$ declines with increasing scattering angle θ . This should be manifested experimentally in an apparent decrease in A_2 with increasing angle θ . Such a phenomenon has actually been observed experimentally in a number of cases.^[189-191] It is manifested as a decrease in the slope of the concentration curves $(Hc/I_\theta)_{\theta=\text{const}}$ with increasing angle θ . In^[191] we reported that the converse phenomenon is observed in the systems poly- β -vinyl-naphthalene-benzene and poly-*p-tert*-butylphenyl-methacrylate-acetone: an increase in the slope of the $(Hc/I_\theta)_{\theta=\text{const}}$ curves with increasing angle θ .* The theories of Albrecht and of Flory and Bueche do not provide for such a behavior of the function $Q(\theta)$. In fact, according to (112) or (113), $Q(\theta) > 1$, and it increases with x for negative z . However, $z < 0$ corresponds to $A_2 < 0$, whereas in the systems described in^[191], the positive slope of the $(Hc/I_\theta)_{\theta=\text{const}}$ curves increased with increasing angle θ .

In line with the fact that the contribution of the high-molecular-weight fractions to the scattering increases with decreasing angle θ , the decrease in A_2 as $\theta \rightarrow 0$, as observed in^[192,193], is probably due to a marked polydispersity inherent in the polyethylene samples. This idea cannot apply to the fractions used in^[191].

*The same behavior of A_2 has been observed in^[192,193] for polyethylene solutions.

Apparently, special cases of intermolecular interaction not covered in the existing theories can be manifested in light scattering. The entire problem thus requires more detailed further study.

In our opinion, the creation of an adequate theory of the second virial coefficient of polymer solutions is still far from completion. The experimental material on this problem also requires a substantial goal-directed expansion.

CONCLUSION

We have discussed the most important applications of the light-scattering method in studying the structure and properties of chain macromolecules. Naturally, most of the space has been devoted to problems on which substantial progress has been made in recent years (the analysis of copolymer structure), or which are of especial interest (the structure of rigid macromolecules). The lack of space has prevented us from taking up a number of applications of light scattering, e.g., the study of polymerization kinetics, the study of intermolecular interactions in the phenomenon of critical opalescence (see^[8]), and several others.

We must bear in mind the fact that, in spite of the value of the information furnished by the light-scattering method, its application in isolation cannot provide an exhaustive solution to the problem of the structure and properties of polymer molecules. This problem is complex, and considerable advances in its individual branches are to be attained by complex studies. The latter must include all of the most important methods of studying the structure of macromolecules. At the same time, as we have tried to show, many special problems can be solved within the framework of the light-scattering method alone.

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